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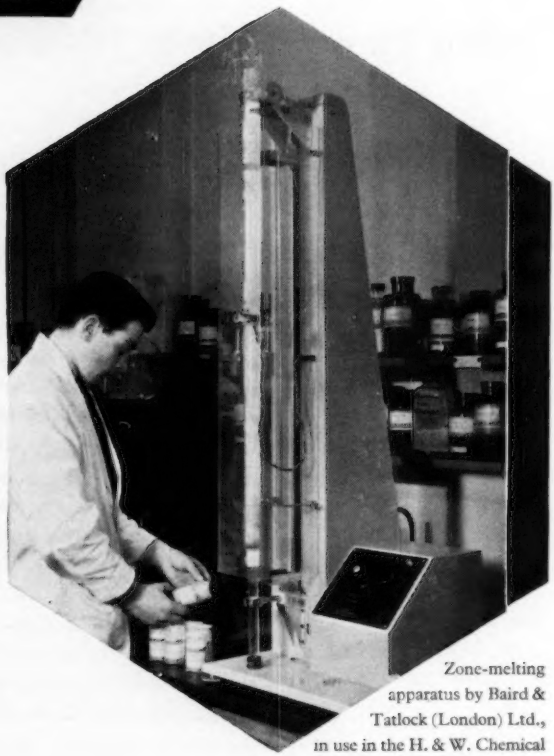

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

1998. **Second Polish Congress of Analytical Chemistry in Warsaw. November 20–23, 1957.** *Chem. Anal., Warsaw*, 1958, **3** (3–4), 187–419.—The following papers are published in Polish unless otherwise stated. **The development of analytical chemistry in Poland,** W. Kemula, 187–192. **Analytical chemistry of traces,** J. Minczewski, 193–206. **Organic analysis on the basis of functional groups,** S. Veibel, 207–221 (in German). **Contribution to the chemistry and analysis of elementary sulphur and some of its compounds,** E. Schulek, E. Kőrös, L. Maros and I. Feher, 223–244 (in German). **Use of perchloric acid in the quantitative determination of some rare metals,** I. P. Alimarin, E. Jen-Yun and I. Puzdrenkova, 245–251 (in Russian). **The oxidation products of nickel dimethylglyoxime,** A. Okač and M. Šimek, 253–267 (in German). **Titrations with chemiluminescent indicators,** L. Erdey, 269–280 (in German). **Spectrophotometric investigation of the products of reactions between s-trinitrobenzene and hydroxides, sulphites, sulphides and cyanides,** F. Čůta, E. Beranek and J. Písecký, 281–289 (in German). **New results in the field of internal electrolysis,** B. Sagortschew, 291–297 (in German). **Spectrochemical analysis of silicates,** I. A. Voinowitch, 299–302 (in French). **The emission of strontium in the oxy-acetylene flame in the presence of calcium, magnesium, barium, sodium, potassium and lithium,** J. Debras and I. A. Voinowitch, 303–312 (in French). **Automation in analytical chemistry,** Z. Zagórski, 313–328. **Gas analysis,** Z. Lada, J. Waclawik and S. Waszak, 329–347. **Automation of gas chromatography with direct measurement of volume,** J. Janák and K. Tesařik, 349–356. **Polarography in the analysis of the alkaloids,** F. Santavy, 357–368 (in German). **A horizontal arc with air-blast as a source of excitation of the spectrum of powdered substances,** A. K. Rusanov and V. G. Khitrov, 369–378 (in Russian). **Organic reagents in chemical analysis,** Z. Marczenko, 379–393. **Progress of complexometry in Czechoslovakia,** J. Kőrbl, 395–402 (in German). **Control of errors in serial analyses,** K. Doerffel, 403–406 (in German). **Polarographic researches on the properties and determination of ter- and quadri-valent cerium,** J. Doležal, 407–419.

1999. **Conference on X-ray analysis, Manchester, April 1958.** Institute of Physics. *Brit. J. Appl. Phys.*, 1959, **10** (3), 116–124.—A summary of the proceedings is published.

2000. **Colloquium on X-ray fluorescence analysis, London, February and April 1958.** Institute of Physics. *Brit. J. Appl. Phys.*, 1959, **10** (3), 105–116.—A summary of the proceedings is published.

2001. **Statistics in chemical analysis. IV. Evaluation of photometric standard measurements and fulfilment of the Beer - Lambert law.** G. Gottschalk and P. Dehmel (Osram-Studienges. f. elektr. Beleuchtung, Berlin). *Z. anal. Chem.*, 1958, **163** (5), 330–338.—This extension of earlier work (*cf. Z. anal. Chem.*, 1958, **163**, 273) is based on the evaluation of the photometric method by means of the extinction coefficient, the procedure factor and the standard deviation. The significance of blank values and their determination are discussed.

B. B. BAUMINGER

2002. **The use of pyridine derivatives in analytical chemistry.** H. Hartkamp (Inst. f. Spektrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck, Germany). *Naturwissenschaften*, 1958, **45** (9), 211.—Chelate formation with metals is common to a great number of pyridine derivatives. Thus pyridine-2:6-dialdoxime yields with Fe^{II} a complex which is intensely red and stable to hot alkali and to EDTA. The same reagent produces with Mn^{3+} in ammoniacal soln. a dichroic colour which is bluish-green in thin layers and red in thick layers. Iron complexes of an intense blue are obtained with picolinic acid thioamide. Blue complexes are also formed with Co^{II} with picolylamine or picolyl methylamine in the presence of NaOH. The chelates of pyridine-2-aldehyde are not themselves highly coloured, but the colours can be greatly intensified by the addition of substances having one or more primary amino groups (*e.g.*, ammonia, hydroxylamine, hydrazine, aliphatic amines). In the same manner chelates of exceptionally intense colour can be produced with pyridine-2-aldehyde and 2-picolylamine. The iron chelate is black - violet, the sparingly soluble nickel chelate a dark red, the cobalt chelate is blue and that of palladium green. The chelate formed with zinc in the presence of NaOH is orange and passes into the organic phase when butanol is added. In this solvent it is red. The copper chelate is brown and changes to blue - grey when the soln. is shaken with air, reverting to brown on standing.

E. KAWERAU

2003. **Dimethylaminodiphenylantipyrinyl carbinol in inorganic analysis.** V. P. Zhivopistsev. *Izv. Vyssh. Ucheb. Zaved., Khim. i Khim. Tekhnol.*, 1958, (1), 65–68; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,178.—The synthesis of the dyestuff dimethylaminodiphenylantipyrinyl carbinol (**I**) is described. The use of **I** for the detection of Zn, Fe, Cd, Bi and Hg and for certain analytical separations is studied. With a 0·03 to 0·04% soln. of **I** in *N* HCl containing 5% NH_4SCN, the detectable minimum for Zn^{2+} is 0·2 to 0·3 μg at a limiting dilution of 1 in $1{\cdot}5 \times 10^6$ and for Fe^{3+} is 0·9 to 1·0 μg at a limiting dilution of 1 in 3×10^6. In both cases no interference is caused by the presence of Al, Cr, Ni, Mn, alkaline-earth or alkali metals. Interfering elements may be removed by treatment with $(NH_4)_2S$. In the presence of I^-, **I** may be used for

the detection of 0·5 μg of Cd and 0·6 μg of Hg, and also for the separation of Cd and Hg from Zn, Fe, Cr, Al, Mn, Co, Ni and other elements (in this case a saturated soln. of **I** in *N* HCl containing 10% KI is used). The detection of Bi by means of **I** in the presence of KI is as sensitive as the cinchonine reaction. **I** may also be used as a collector for the separation of elements that form complex thiocyanate anions (*e.g.*, Zn, Fe, Hg and Co).

C. D. KOPKIN

2004. **7-Amino-1-methylphenoxaz-3-one as an analytical reagent.** E. Růžička (Chem. Inst. of High Pedag. School, Olomouc, Czechoslovakia). *Chem. Listy*, 1958, **52** (9), 1716–1719.—7-Amino-1-methylphenoxaz-3-one (orcirufamine) (**I**) has been found to be a sensitive reagent for the detection of Sn^{2+}, Ti^{3+}, Cr^{2+}, ClO_3^-, BrO_3^- and IO_3^- in strongly acid HCl soln. The halogenation of **I** with chlorine or bromine in neutral and slightly acid soln. has been studied potentiometrically. *Detection of Sn^{2+}, Cr^{2+} and Ti^{3+}.*—The red - violet colour of **I** soln. (0·005 g of **I** in 100 ml of 96% ethanol) in 2 *N* HCl is discharged in the presence of stannous, titanous and chromous salts. The sensitivity on filter-paper is 1 in $10^{5\cdot4}$ for Sn^{2+} and 1 in 10^6 for Ti^{3+}. *Detection of Cl and Br.*—In the presence of Cl the reagent is decolorised; in the presence of Br a brown - red ppt. is formed; the reaction must be carried out in a slightly acid or neutral soln. The sensitivity is 1 in 10^6 for Cl and 1 in 10^4 for Br on filter-paper. Interference is caused by H_2O_2, $S_2O_3^{2-}$ and ClO^-. Bromine and chlorine waters can be titrated with a 10^{-4} *M* ethanolic soln. of **I**. Chloride does not interfere; ClO_3^-, BrO_3^-, ClO^-, IO_3^-, NO_2^-, H_2O_2 and other oxidising agents interfere.

J. ŽÝKA

2005. **Phenylhydrazinodithioformic acid as an analytical reagent.** A. Musil and W. Haas (Inst. für anorg. u. anal. Chem., Univ., Graz, Austria). *Mikrochim. Acta*, 1958, (6), 756–765.—The ammonium salt of phenylhydrazinodithioformic acid is easily prepared in a pure form and gives difficultly soluble ppt. with many metals. To prepare the reagent, dissolve 21·6 g of phenylhydrazine and 18 g of carbon disulphide in ethanol. Pass a moderate stream of NH_3 gas through the soln. After 15 min. filter off, with suction, the dull white crystals of the ammonium salt, which are insol. in ethanol. Wash the ppt. with ethanol and ether. The substance is easily sol. in H_2O, but is stable in the atmosphere for only a few hours. A simple semi-quant. method for Ag is based on the changes in colour produced with different amounts of Ag. The Pb compound is suitable for gravimetric determination; Cu is determined similarly to Ag in about 10 min.

D. F. PHILLIPS

2006. **The origins of quantitative inorganic analysis.** R. E. Coulson (Imperial Smelting Corporation Limited, St. Andrew's Road, Avonmouth, Bristol, England). *Talanta*, 1958, **1** (3), 256–262.—An historical study.

P. D. PARR-RICHARD

2007. **Kofler's glass-powder method in the quantitative analysis of binary mixtures.** M. Brandstätter-Kuhnert and A. Martinek (Pharmakogn. Inst., Univ., Innsbruck, Austria). *Mikrochim. Acta*, 1958, (6), 803–811.—The assumption that the temp. at which the refractive index of a mixed melt of two constituents is equal to that of a glass of given refraction varies linearly with concn. (Kofler, *Mikrochem.*, 1937, **22**, 241) is not always valid. A straight line in the temp. - concn. diagram can be expected only if it is assumed that the temp. coeff. of the refraction are equal for both components and that the refraction at constant temp. is a linear function of the concn. This applies mainly to substances which, because of chemical relationship, also have similar physical properties. In other cases consideration must be given to curves whose curvature is dependent (*i*), on the magnitude of the differences of the two temp. coeff., and (*ii*), on the deviations in the n^t - concn. diagram. Extreme curvature of curves may only be expected in the latter case.

D. F. PHILLIPS

2008. **Theory of neutralisation of indicators in heterogeneous phase and new applications of some of the eosin group.** F. Sierra and C. Sánchez-Pedreño (Murcia Univ., Spain). *Inf. Quim. Anal.*, 1958, **12** (4), 91–103.—The mechanism of action of adsorption indicators is considered, with particular reference to the influence of the acidity of the external aq. phase. Procedures are described for the determination with Ag^+ of Cl^-, with eosin or phloxin as indicators, and of Cl^- or Br^- with tri-iodofluorescein or erythrosine B, and the determination of Ag^+ with Cl^-, Br^-, I^- or SCN^-, and eosin.

L. A. O'NEILL

2009. **Use of brucine as an oxidation - reduction indicator in cerimetry.** G. Gopala Rao and T. P. Sastri (Andhra University, Waltair, S. India). *Talanta*, 1958, **1** (3), 213–215.—The stability of the indicator in H_2SO_4 depends on the concn. of the acid and of the brucine; a 0·1% soln. in 3 *N* H_2SO_4 or in 2 to 3 *N* acetic acid is satisfactory. For the titration of Fe^{II} in 0·5 to 8 *N* H_2SO_4 with 0·01 to 0·1 *N* $Ce(SO_4)_2$ brucine works well even in the absence of PO_4^{3-}, and tungstic acid does not interfere. Up to 1% of Ni may be present, but > 0·1% of Co masks the colour. For the titration of Fe^{3+} in HCl, add H_3PO_4 to improve the end-point; the colour is not stable. For the determination of $Fe(CN)_6^{4-}$, the sample must be diluted sufficiently to prevent colour masking by $Fe(CN)_6^{3-}$; the concn. of H_2SO_4 should be $\geq$ 4 *N*, preferably 0·5 to 1·0 *N*.

P. D. PARR-RICHARD

2010. **The use of fluorescein complexone.** J. Körbl, F. Vydra and R. Přibil (Res. Inst. for Pharm. and Biochem., Czech. Acad. Sci., Prague). *Talanta*, 1958, **1** (3), 281–282.—For the complexometric titration of Ca, Sr and Ba, with fluorescein complexone as indicator (Calcein, Fluorexone), the alkalinity of the soln. to be titrated is usually adjusted with NaOH. It is shown that fluorescein complexone gives fluorescence reactions with some alkali metals, particularly Na; K gives the least response. Hence to improve end-point quality, KOH should be used to adjust alkalinity, particularly for Ba and indirect SO_4^{2-} determinations.

P. D. PARR-RICHARD

2011. **Complexone-type metallochromic indicators.** J. Körbl, V. Svoboda and D. Terzijská (Pharm. and Biochem. Res. Inst., Prague). *Chem. & Ind.*, 1958, (38), 1232–1233.—New indicators have been prepared by condensation of sulphophthalein dyes with HCHO and either ββ′-iminodipropionic acid (**I**) or N-(β-carboxyethyl)glycine (**II**). The latter are less sensitive than analogous compounds from iminodiacetic acid; the **I** derivatives resemble those from β-alanine. Metallochromic properties decrease as follows—iminodiacetic acid > **II** > glycine (and other α-amino acids) = **I** > β-alanine.

P. D. PARR-RICHARD

2012. **New azopyridines as chelatometric indicators.** L. Sommer and M. Hniličková (Inst. f. Anal. Chem., Univ. Brno, Czechoslovakia). *Naturwissenschaften*, 1958, **45** (22), 544.—The only indicator of this group so far used is 1-(2-pyridylazo)-2-naphthol (PAN) (**I**). The authors synthesised in addition 2-(2-pyridylazo)chromotropic acid (**II**), 2-(2-pyridylazo)-1-amino-8-hydroxynaphthalene-3:6-disulphonic acid (**III**) and 4-(2-pyridylazo)resorcinol (**IV**). The azopyridines react in neutral or weakly alkaline soln. with Pb^{II}, Zn^{II}, Cd^{II}, Cu^{II}, Ni^{II}, Co^{II}, Hg^{II}, UO_2^{2+}, Pd^{II}; **II** and **IV** in addition react with Sc^{III}, Y^{III}, La^{III}, In^{III}, Nd^{III}, Er^{III}, Zr^{IV} and Ti^{IV}. Only **II** reacts with Be^{II} and **IV** also reacts with Ce^{III} and Th^{IV}. The chelates of Cu^{II} and Pd^{II} are stable in the presence of 0·1 *N* HNO_3. The only reaction of interest in an alkaline medium is that of Pd^{II}. Bivalent metals give more marked reactions than polyvalent cations. Both **II** and **III** are recommended for the titration of Cu^{II} with EDTA in acetate buffer or weakly ammoniacal soln.; for **II** the end-point is from burgundy red to orange or from blue - violet to pink - orange when ammonia is present, for **III** the end-point is from blue to pink. Indicator **IV** can be used in weakly ammoniacal soln. or with hexamine as buffer for the EDTA titration of Zn^{II} with a sharp end-point of red to yellow at pH > 5. For Pb^{II} the end-point is exceedingly sharp and Bi^{III} gives a change from red to yellow when titrated in 0·1 *N* HNO_3; Cu^{II} is best titrated in acetate buffer and shows an end-point from burgundy red to green; Cd^{II} can also be titrated with this reagent. The indicators **II**, **III** and **IV** are all superior to **I** because of their sharp end-points and the solubility of their reaction products, the chelate of **I** with Cu^{II} being insoluble.

E. Kawerau

2013. **Eriochrome blue SE as indicator in chelatometric titrations.** A. A. Abd El Raheem and Abdel-Aziz M. Amin (Min. of Pub. Health Lab. and Nat. Res. Centre, Cairo, Egypt). *Z. anal. Chem.*, 1958, **163** (5), 340–344 (in English).—The use of Eriochrome blue SE (**I**) as indicator for the titration of Mn, Zn, Ni, Cd, Pb and Mg with EDTA soln. (**II**) has been investigated. The sensitivity of the detection of the end-points has been determined by mixing equal volumes of 0·01 *M* soln. of the metal salt under test and 0·01 *M* soln. of **II**. The pH of the soln. mixture is adjusted to 10 by the addition of a buffer. To 0·03 ml of **I** is added 0·03 ml of metal salt on the spot-plate. A clear blue colour is obtained in all cases, except with cobalt when an irreversible rose colour develops. The detection limits of these metals have been estimated and the standard deviations and probable errors are 7·3 μg and 4·9 μg for Mn; 7·0 μg and 4·6 μg for Zn; 11·4 μg and 7·6 μg for Ni; 8·5 μg and 5·2 μg for Cd; 17·5 μg and 11·7 μg for Pb; and 3·1 μg and 2·0 μg for Mg.

B. B. Bauminger

2014. **Indophenol complexones: a new group of metallochromic indicators.** J. Körbl and V. Svoboda (Pharm. and Biochem. Res. Inst., Prague). *Chem. & Ind.*, 1958, (38), 1233–1234.—Twelve new indicators have been prepared indirectly as water-sol. sodium salts. Aq. acid soln. are orange to red, changing to blue between pH 4 and 6. At pH 3·5, all 12 give deep blue or violet chelates with Zr^{4+}, Bi^{3+}, Th^{4+}, Sc^{3+}, Fe^{3+} and Al^{3+}, and three will also react with Ni^{2+}, Cu^{2+} and Zn^{2+}. Reaction with EDTA is slow for complexes of Fe^{3+}, Zr^{4+}, Ni^{2+} and Al^{3+}, but instantaneous for those of Th^{4+}, Bi^{3+}, Sc^{3+}, Cu^{2+} and Zn^{2+}. Chelates formed in alkaline soln. are masked by the colour of the indicator. The indoaniline analogues are also being studied.

P. D. Parr-Richard

2015. **Titrimetric analysis with chloramine T. I. The status of chloramine T as a titrimetric reagent.** E. Bishop and V. J. Jennings (Washington Singer Lab., Univ., Exeter, England). *Talanta*, 1958, **1** (3), 197–212.—Previously described work with chloramine T (**I**) is unsatisfactory, the methods given being inadequate. **I** is generally only suitable for oxidation of halides. Solid and soln. are stable for several months if stored in dark glass. **I** can be purified to 99·5% by recrystallisation, and standardised with As^{III} as follows. Pipette 50 ml of 0·05 *M* As^{III} soln. into a bottle, add 40 ml of 10 *M* HCl and 20 ml of 1·0 *M* KBr; the final titration vol. is 200 ml. Titrate with 0·05 *M* **I** to within 0·1 ml of the end-point, add 4 drops of 0·1% aq. rosaniline hydrochloride, and titrate split-dropwise to a purple end-point, shaking after each addition.

P. D. Parr-Richard

2016. **Iodine chloride as volumetric reagent. II. Determination by sodium acetate method.** Balwant Singh and G. P. Kashyap (Chem. Dept., Punjab Univ., Hoshiarpur, India). *Z. anal. Chem.*, 1958, **163** (5), 338–340 (in English).—The use of iodine chloride in the volumetric determination of reducing agents at pH 6·5 to 7·5 in a Na acetate-buffered soln. is described. Chloroform is used as an indicator and becomes violet at the end-point, owing to the liberation of iodine. Procedure and results are given for the determination of As_2O_3, antimony potassium tartrate, hydrazine sulphate, quinol, Na_2SO_3, $SnCl_2.2H_2O$ and $K_4Fe(CN_6).3H_2O$.

B. B. Bauminger

2017. **Instrumental methods in non-aqueous titrimetry.** J. T. Stock and W. C. Purdy (Dept. of Chem., Univ., College Park, Md., U.S.A.). *Lab. Practice*, 1958, **7** (9), 523–525.—Photometric, thermometric, coulometric and amperometric arrangements and procedures for following non-aq. titrations are reviewed. (35 references.)

W. J. Baker

2018. **The theory of gas chromatography and some of its applications.** A. I. M. Keulemans and G. W. A. Rijnders (Koninkl. Shell-Lab., Amsterdam). *Naturwissenschaften*, 1958, **45** (13), 301.—The principles underlying the processes of separation in liquid - solid, liquid - liquid, gas - solid and gas - liquid chromatography are discussed. Detailed consideration is given to "ideal" conditions and "non-ideal" conditions of operation. As a practical example, the separation of a synthetic mixture of gases resembling cracking gas in composition is described, with different liquids for the stationary phase.

E. Kawerau

2019. **The practical application of chromatographic theory to analytical and preparative separations by ion-exchange elution.** F. W. Cornish (Anal. Chem. Group, A.E.R.E., Harwell, Berks., England). *Analyst*, 1958, **83**, 634–642.—The application of the theoretical principles of chromatographic separation on ion-exchange columns to the selection of operating conditions for the separation of any pair of elements to any desired degree of purity is discussed, and data are presented in graphical form from which such operating conditions can be deduced.

A. O. Jones

2020. **Scope of the nitroprusside reagent in paper chromatography.** E. Hofmann and A. Wünsch (Inst. für Agrikulturchem., Tech. Hochschule, München in Weihenstephan). *Naturwissenschaften*, 1958, **45** (14), 338.—The spray reagent should be freshly prepared and is a mixture of 2 ml of 5% sodium nitroprusside soln., 1 ml of 10% NaOH soln., 5 ml of H_2O_2 (3%) and water to 15 ml. The substances that react are cyanamide (violet), dicyandiamide (carmine), guanylurea (yellow - orange), guanidine (red - orange), arginine (rose), creatine (carmine), creatinine (yellow - brown - orange), arcaine (faint rose), agmatine (rose), guanidinoacetic acid (carmine), thiourea (red - violet) and urea (pale rose). Subsequent acidification of the chromatogram with acetic acid turns the colour of dicyandiamide to yellow - orange, creatinine to lemon yellow and thiourea to a light blue. All other colours except that of cyanamide are discharged. E. KAWERAU

2021. **Application of ion-exchange materials in analytical chemistry.** J. Inczédy (General Chem. Inst., Polytech. Univ., Budapest). *Magyar Kém. Lapja*, 1958, **13** (7–8), 293–299.—A review, with 120 references. G. SZABO

2022. **Ion-exchange resins in the radiochemical analysis of natural objects. I. Concentration and separation of natural radio-elements by means of the cationite KU-2.** L. A. Kapatsinskaya and N. G. Sȳromyatnikov. *Vestn. Akad. Nauk, KazSSR*, 1958, (4), 60–66; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,173.—All natural radioactive elements are quantitatively adsorbed by the cationite KU-2 from neutral soln. and from a soln. containing up to 5% HCl. At pH 7 to 8, U, Ra and Th are also quantitatively adsorbed from natural waters. With a 6-cm column of diam. 1·3 cm, the rate of filtration may be as much as 25 ml per min. per sq. cm cross-section without affecting the completeness of the adsorption of the micro-components. The eluting soln. are used at a rate of passage of 2 ml per min. To remove Ac from Th, wash the column, saturated with the radioactive elements, with 20% HNO_3 (200 ml), all the Ac being extracted. Then extract the Th by washing the column with 5% oxalic acid soln. (50 ml). An analogous method is used for the separation of U and Th. To separate the thorium isotopes, pass the acid soln. (5 or 10% in HCl or HNO_3) containing other radioactive elements through the column at a rate of up to 50 ml per min. Wash the column with 20% HNO_3 to remove all the radioactive elements except the thorium isotopes, and elute these with 5% oxalic acid soln (50 ml). For the determination of ^{228}Ra, the isotopes of Ra and U must be removed. Wash the column containing the radioactive elements with 5% oxalic acid soln. (80 ml) to remove U, isotopes of Th, Bi and Ac, and then with water, and extract the lead isotopes by the passage of 60 ml of 5% ammonium acetate soln., and then Ra either by 10% NH_4Cl soln. (250 ml) or 20% HNO_3 (250 ml). The Pb obtained is slightly contaminated with Ra. C. D. KOPKIN

See also Abstracts—**2035**, 2-(-2-Hydroxy-5-methoxyphenylazo)-4-methylthiazole as a reagent. **2042**, **2110**, Mercaptoquinolines as reagents. **2222**, Preparation of standard soln. of BrCl. **2412**, Contributions of microwave spectroscopy to chemistry.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

2023. **Polarography of metal - thiosulphate complexes.** D. G. Davis (Georgia Inst. of Technol., Atlanta 13, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1729–1732.—The polarography of various metal ions in thiosulphate media has been studied to establish analytical methods and to determine the co-ordination numbers and dissociation constants of the metal ion complexes. Cadmium, Pb and Cu^{I} gave waves which were reversible and determinable, but As^{III}, Co^{II}, Mn and Zr gave no useful waves. K. A. PROCTOR

2024. **Elimination of the phenomenon of adsorption by precipitated ferric hydroxide in the polarographic determination of copper, cadmium, nickel and zinc in ammoniacal solutions.** M. Papadopol. *Rev. Chim., Bucharest*, 1958, **9** (7–8), 464–466.—The method is based on the fact that there is no adsorption by $Fe(OH)_3$ of these metal ions if the sum of the concn. of aq. NH_3 and NH_4Cl is $\leq 3\ M$. *Procedure*—The finely ground material (0·2 to 0·4 g) is dissolved by treatment with five times its wt. of $KClO_3$ and 2·5 to 5 ml of HNO_3 (1 : 1). The soln. is evaporated to dryness, the residue is dissolved in 2 to 3 ml of conc. HCl, re-evaporated to dryness, moistened with 1 ml of conc. HCl and dissolved in a few ml of water. The soln. is transferred to a 100-ml flask with 25 ml of water and NH_4Cl soln. (5 *M*), 20 ml of aq. NH_3 (10 *M*) and 4 ml of gelatin soln. (0·5%), then 4 ml of a saturated soln. of Na_2SO_3 is added, and the soln. is diluted to 100 ml. The mixture is shaken and, after the $Fe(OH)_3$ has settled, a convenient quantity of the clear soln. is removed for the polarographic determination of Cu with an applied e.m.f. of 0 to 0·7 V and of 0·6 to 0·9 V for Cd. In another cell, 5 ml of the soln. is diluted with 5 ml of water, mixed and analysed for Ni and Zn between 1 and 1·7 V. Standard soln. are prepared in the usual manner without Fe. Nickel and Zn cannot be determined by this method if Co is present. H. SHER

2025. **Automatic spectrophotometric titration of fluoride, sulphate, uranium and thorium.** O. Menis, D. L. Manning and R. G. Ball (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1772–1776.—The spectrophotometric procedures described permit from 6 to 50 μg of F^- or SO_4^{2-}, 12 to 200 μg of U^{4+} and 2 to 60 μg of Th to be determined in a glass cell (3 in. × 2 in. × 1·5 in.), with a coeff. of variation of 4, 5, 3 and 1%, respectively. Quercetin soln. (0·1%, w/v) is used as indicator for the titration of Th with 0·001 *M* EDTA (disodium salt) at pH 3 and 422 mμ; alizarin red S for the titration of F^- with 0·0005 *M* $Th(NO_3)_4$ at $\simeq$ pH 3 and 520 mμ; and thoron for the titration of SO_4^{2-}, in a mixture (2 : 1, by vol.) of *iso*amyl alcohol and methanol, with 0·00125 *M* $Ba(ClO_4)_2$ at 520 mμ. The U^{4+} are titrated in dil. H_2SO_4 with 0·1 *M* $Ce(SO_4)_2$ at 340 mμ. The titrations are made in a Warren Spectracord modified to include a time-drive attachment, a titrant-feed assembly, and a device permitting access to the sample compartment without removing the stirrer and burette tip. W. J. BAKER

2026. **Mercurimetric titrations with redox indicators. II. Determination of thiocyanate, cyanide**

and mercury(II) ions. J. Bognár (Tech. Univ. for Heavy Indust., Miskolc, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (1), 27–35.—This is an English translation of the paper abstracted in *Anal. Abstr.*, 1958, **5**, 3661. R. E. ESSERY

2027. **Study of the absorption spectra of the 8-hydroxyquinolinates of certain rare elements.** I. P. Alimarin, E. S. Przheval'skiĭ, I. V. Puzdrenkova and A. P. Golovina. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 152–160; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,181.—The extraction of the 8-hydroxyquinolinates of Ce^{3+}, Ce^{4+}, Ti^{4+}, Zr^{4+}, Nb^{5+}, Th^{4+} and Ta^{5+} with various organic solvents is studied. The 8-hydroxyquinolinate of Ti is quantitatively extracted at pH 1·5 to 2·5, of Ce^{4+} at pH 9·9 to 10·6, of Zr, Th and U at pH 4·6, of Nb at pH 6·9 and of Ta at pH 6 to 7. The absorption max. of the $CHCl_3$ soln. for Zr, Th, Ce^{3+}, Ti, Ta and Ce^{4+} lie at 393, 383, 395 to 400, 388 and 495 mμ, respectively. On the basis of these data, a spectrophotometric method is evolved for the determination of Ce and Ti in the presence of other elements. To determine Ce (Ce^{3+} or Ce^{4+}), add to the acidified soln. (containing 20 to 300 μg of Ce in 8 or 10 ml) in a separating funnel, a 1% ethanolic soln. of 8-hydroxyquinoline (1 ml), phenolphthalein (2 or 3 drops), conc. aq. NH_3 soln. dropwise to an alkaline reaction, and 5% aq. NH_3 soln. (1 to 1·5 ml) to pH 9·9 to 10·6. Extract the cerium compound with two 5-ml portions of $CHCl_3$ (shaking for 5 min.), separate the $CHCl_3$ layer and measure the extinction at 495 mμ, with $CHCl_3$ as comparison soln. The sensitivity of the reaction is 1 μg of Ce per ml. The mol. extinction coeff. is ≃ 6700. Beer's law is obeyed for 20 to 300 μg of Ce in 8 or 10 ml of soln. To determine Ce in the presence of Th and the rare earths, measure the extinction of the $CHCl_3$ extract at 540 mμ (the 8-hydroxyquinolinates of Th and the rare-earth elements do not absorb under these conditions). Interference due to the presence of Ti may be eliminated by adding EDTA (disodium salt), in the presence of which the titanium 8-hydroxyquinolinate is not extracted with $CHCl_3$ at pH 9·9 to 10·6. The method described has been tested on a synthetic mixture containing Ce, Th, La, Nd and Pr, with a composition approximately that of monazite. C. D. KOPKIN

2028. **Tritium and paper chromatography.** A. T. Wilson (Div. of Nuclear Sci., D.S.I.R., Lower Hutt, New Zealand). *Nature*, 1958, **182**, 524.—Tritium-labelled compounds on a paper chromatogram will not mark a superimposed film, owing to absorption of the weak β-particles by the paper. By soaking this in a liquid scintillator, the β-particles are converted into light which registers on the film. The quality of the radio-autograms produced compares favourably with those obtained with ^{14}C. A typical experiment on the role of H in photosynthesis is described, and other applications are discussed. P. D. PARR-RICHARD

2029. **System for counting tritium as water vapour.** W. F. Merritt (Atomic Energy of Canada, Ltd., Chalk River, Ontario). *Anal. Chem.*, 1958, **30** (11), 1745–1747.—Tritiated water (10 μl) is pipetted into a sample tube which is connected by means of a short line and valve to a vacuum system and a heated circulating counting device (illustrated). The sample is distilled within 5 min. into the counter (previously flushed with pure water) and technical methane is used to sweep in any residual vapour. When the pressure in the counter is 1 atmosphere, the valve is closed and the homogeneous gas is counted (10^3 to 10^3 times the background count) at 90°. The tritium content is read from a calibration curve. The method is rapid and accurate to within ± 2%. The sensitivity of the counter (3×10^4 μC, *i.e.*, 0·03 μC per ml) could be greatly increased by shielding. J. P. STERN

2030. **Spectrographic determination of nitrogen impurity in argon.** V. I. Dianov-Klokov, V. A. Kolbasov and K. N. Lemarin'e. *Kislorod*, 1958, (2), 49–51; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,733.—The analysis is carried out on an improved apparatus, described previously (*Ref. Zhur., Khim.*, 1956, Abstr. No. 78,476). The charge accumulation method is used, which decreases the probable error of the reading and increases the light sensitivity of the instrument. Diagrams are given of the apparatus and the photo-electric analyser. The analysis is effected on the nitrogen band at 3998 A and the argon doublet 4511 - 4522 A in the concn. intervals 0·01 to 0·1 or 0·05 to 0·5% of N. The error of the analysis is ± 10%. Up to 0·2% of O does not interfere. C. D. KOPKIN

2031. **Photo-electric determination of nitrogen in argon.** O. P. Bochkova, L. P. Razumovskaya and V. G. Sagaldak. *Kislorod*, 1957, (4), 24–27; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,304.—The apparatus consists of a discharge tube, a HF generator for exciting the radiation of A, and a condenser which projects the light from the discharge tube on to the photo-cathode of a photo-multiplier; in front of the photo-multiplier is a filter which passes the radiation in the portion of the spectrum characteristic of N. For purification from O, the gas is passed through copper foil at 400°. Samples of argon with a known content of N are used as standards. From 0·01 to 0·6% of N can be determined. The analysis takes ≯ 1 min.; the time required for washing the apparatus is ≃ 10 min. The coeff. of variation of the determination is ± 4%. The analytical results agree well with those of the lithium method. C. D. KOPKIN

2032. **Conductimetric determination of sodium and potassium in the presence of each other.** V. Novák and A. Krajina (High School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (8), 1506–1512.—A simple and rapid method for the conversion of chlorides of potassium and sodium into hydroxides ($Ag_2O + 2Cl^- + H_2O = 2OH^- + 2AgCl$) is described. The soln. of the hydroxides of both elements in ethanol is titrated conductimetrically with $HClO_4$ which enables K and Na to be distinguished. *Procedure*—To the soln. of KCl and NaCl (5 ml) add an amount of moistened Ag_2O more than equiv. to the Na and K and shake vigorously for 10 min. Filter off the Ag_2O and AgCl on a glass filter G4 into a 200-ml flask, wash the ppt. with H_2O (5 ml) and ethanol and dilute the filtrate with ethanol to vol. Titrate 50 ml of this soln. with 0·1 *N* $HClO_4$ (ethanolic soln.). Samples containing Na and K in the ratio 1:5 or 5:1 can be determined with a max. relative error of ± 2%. When the ratio of either element increases to 10:1, the error increases to ± 5%. J. ZÝKA

2033. **Flame-photometric determination of alkali-metal oxides in raw materials, slimes and clinker.** Z. A. Kel'tseva. *Tsement*, 1958, (2), 19–21; *Ref. Zhur., Khim.*, 1958, (24), Abstr. No. 81,286.—A flame photometer, with separate photo-elements

reacting to the emission of K and Na, interference filters and a special photo-element to compensate for the emission of Ca (*Ref. Zhur., Khim.*, 1953, Abstr. No. 3488), is used for the determination of Na and K in clays and other materials containing up to 4% of Na_2O and 7% of K_2O. The air-acetylene flame is used. The influence of Al, Fe and Mg on the accuracy of the determination of Na and K is not established; neither is the mutual influence of Na and K. For the determination, treat 0·5 g of sample with HF (10 ml) in the presence of 7 or 8 drops of H_2SO_4. After removal of the acids by heating, extract Na and K with hot water (500 ml); with less water (250 ml) a certain amount of Na remains unextracted in some of the samples. The deviation of results of separate measurements is $\not< \pm 4{\cdot}5\%$ for Na_2O and $\pm 5{\cdot}8\%$ for K_2O.

C. D. KOPKIN

2034. **Reactions of copper ions with thiosemicarbazide.** V. N. Podchaĭnova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 183–197; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,208.—In an acid medium containing Cu^{2+}, thiosemicarbazide (**I**) forms a coloured compound of composition Cu:**I** = 1:2. Aq. soln. of this compound are stable in the light for 2 hr.; longer standing causes separation of crystals and decolorisation of the soln. The stability is maintained at $< 60°$. Beer's law is obeyed for the concn. interval $1{\cdot}5 \times 10^{-4}$ to 3×10^{-3} moles of Cu per litre at pH $\not> 7$. To determine Cu in nickel or zinc alloys, dissolve 0·5 to 1·0 g of sample in 10 or 15 ml of a mixture of dil. HNO_3 and HCl (1:1). Evaporate the soln. almost to dryness, add 0·5 or 1·0 ml of conc. HCl and 5 or 6 ml of water to the residue and warm to dissolve the salts. Dilute the resulting soln. to 50 or 100 ml, and add 5 or 6 ml of a 0·2% soln. of **I** in 2 *N* H_2SO_4 to a 2- or 5-ml aliquot. Dilute with 2 *N* H_2SO_4 to 25 or 50 ml and mix, and measure the extinction, with a red filter. To construct a calibration curve, use samples of zinc or nickel alloys with known copper content. To determine Cu in gold alloys, dissolve the sample (0·05 to 0·07 g) by warming in 5 or 10 ml of a mixture of HNO_3 and HCl (1:1) and make up to 50 ml. To 1 ml of the resulting soln. in a 10-ml cylinder add water (2 ml) and a 1% soln. of **I** (2 ml), and mix. In a similar cylinder place water (2 ml) and a 1% soln. of **I** (2 ml), and add a standard soln. of Cu^{2+} from a micro-burette until the colours match; level off the volumes of liquid in the cylinders by adding water, and calculate the concn. of Cu. The results differ only very slightly from those obtained by other methods. A determination takes 25 to 35 min. Procedures are also described for the determination of Cu in soln. of pure salts and in the presence of Ni, Co, Fe, Ir, Ag and Au. Chromium interferes in the photometric determination of Cu.

C. D. KOPKIN

2035. **Studies on 2-(2-hydroxy-5-methoxyphenylazo)-4-methylthiazole as an analytical reagent. I. Synthesis and the colour reaction with metal ions.** Tadashi Yanagihara, Nobuhisa Matano and Akira Kawase (National Res. Inst. for Metals, Meguro-ku, Tokyo). *Japan Analyst*, 1958, **7** (8), 496–500.—2-(2-Hydroxy-5-methoxyphenylazo)-4-methylthiazole (**I**) reacts with Cu to give a green colour at pH 2 to 7, with Fe^{3+} to give violet at pH 3 to 7, with Ni to give blue at pH 3 to 7 and with Co to give blue at pH 3 to 7 in a weakly acid soln.; in a neutral soln. it gives a blue colour with Pb, Hg, Zn, Mn and Cd. The coloured chelates are extractable with CCl_4, $CHCl_3$, benzene, ethyl acetate and *iso*amyl alcohol. **I** appears to be suitable for the detection and determination of Cu, Fe^{3+}, Ni, Co and Zn. The colours of other metal complexes are unstable.

II. Determination of copper. Tadashi Yanagihara, Nobuhisa Matano and Akira Kawase. *Ibid.*, 1958, **7** (8), 500–505.—The green chelate of **I** with Cu has max. absorptions at 425 and 634 mμ and the latter is stable at pH 5, obeying Beer's law for < 30 μg per 25 ml. Copper (< 10 μg) is extracted with *iso*amyl alcohol in the presence of **I** (0·0005 *M* in ethanol) (2 ml) at pH 8 (borax buffer) and determined colorimetrically at 634 mμ. **I** is also useful as an indicator for EDTA titration of Cu at pH 5 to 7.

K. SAITO

2036. **Colorimetry of copper with sodium azide.** Teruyuki Kanie (Nagoya Municipal Ind. Res. Inst., Rokubancho, Atsuta-Ku). *Japan Analyst*, 1958, **7** (8), 510–512.—In a weakly acid soln. (pH 2·5 to 6·4) NaN_3 reacts with Cu to give a yellow colour (max. absorption, 385 mμ); the extinction at 375 mμ obeys Beer's law for $< 0{\cdot}4$ mg of Cu per 50 ml in the presence of 50 mg of NaN_3. The presence of Fe^{3+}, U, Mo, Ni, Al, Ti, Ag, Hg, Sb, Zr, NH_4^+, CN^-, oxalic and phosphoric acids causes interference. Ferric ions are masked with F^-.

K. SAITO

2037. **New rapid method for the gravimetric determination of copper.** J. Dick and F. Mihai (Inst. Politeh., Timişoara, Romania). *Acad. R.P.R., Baza Cercet. Ştiinţ. Timişoara, Stud. Cercet. Ştiinţ., Ser. I*, 1957, **4**, 67–71.—Copper is pptd. as the Cu dilituarate of formula $(C_4H_2O_2N_2NO_2)_2Cu.8H_2O$. The determination is carried out by dissolving 0·1 to 0·2 g of the unknown in 50 to 60 ml of water and 20 to 25 ml of 95% ethanol and pptg. with 40 to 50 ml of 2% dilituric acid soln. The ppt. is light blue and insol. in water, ethanol and ether. The soln. is decanted through a glass or porcelain crucible and the ppt. washed, first with a soln. containing 40% of 95% ethanol, and finally 4 to 5 times with 2 ml of diethyl ether, then dried in a vacuum-desiccator for 5 to 10 min. Small quantities of ammonium salts do not interfere, but Cd, Co, Ni, Pb and Zn do. The sensitivity is 1·5 μg of Cu per ml.

CHEM. ABSTR.

2038. **Photometric determination of copper as copper(II) aminoacetate.** M. Ziegler (Anorg.-chem. Inst., Univ., Göttingen). *Z. anal. Chem.*, 1958, **163** (3), 197–200.—Copper in copper alloys is determined spectrophotometrically as its aminoacetate with a standard deviation of 0·15%. *Procedure*—A suitable weight of sample is dissolved in conc. HNO_3 and the soln. is evaporated to $\simeq 5$ ml and diluted to 20 ml. The soln., together with 25 ml of 10% aq. glycine containing 4% of Na citrate, is diluted to 100 ml, and its extinction is measured at 735 mμ. If Sn is present, stannic acids must be filtered off. Whilst Co, Zn, Sn^{IV} and Mn do not interfere, Al, Fe, Ni and Cr^{III} interfere when present in fairly large amounts. However, the presence of Fe and Ni in most copper alloys ($< 1\%$ and $< 10\%$, respectively) is not expected to cause interference.

J. H. WATON

2039. **Flame-photometric determination of copper.** H. Bode and H. Fabian (Anorg.-chem. Inst., Tech. Hochsch., Hanover). *Z. anal. Chem.*, 1958, **163** (3), 187–196.—Factors influencing the determination are studied. The addition of wetting agents or of water-miscible organic solvents (particularly acetone) improves the sensitivity. In further tests on an aq. acetone soln. of Cu, HCl, $HClO_4$ and HNO_3 in concn. $> N$ and H_2SO_4 at concn. $> 0{\cdot}25$ *N*

are found to lower the sensitivity. Aluminium, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Na, Ni and Sn do not interfere when present in up to a 50-fold excess. The results of copper determinations obtained on various alloys show good agreement with theoretical values. J. H. WATON

2040. **Iodimetric determination of a mixture of cuprous and cupric ions.** S. A. Kiss (Chem. Combine of Borsod, Hungary). *Magyar Kém. Lapja*, 1958, **13** (7–8), 305–306.—Oxidation of Cu^{+} with iodine can be completed by using an alkali tartrate which forms a complex with Cu^{2+}. An aliquot of the soln. of Cu^{+} and Cu^{2+} is transferred to a flask which contains an alkali tartrate with a known quantity of iodine, the excess of which is titrated with $Na_2S_2O_3$ soln. The consumption gives the value for Cu^{+}. The complex is then destroyed with strong acid, KI is added and the liberated iodine is titrated. The titre gives the total Cu content. This method is used for copper liquors that have been employed for CO absorption in synthetic ammonia manufacture. G. SZABO

2041. **Identification of copper and cadmium without the use of potassium cyanide.** H. G. Husted (Regis College, Weston, Mass.). *J. Chem. Educ.*, 1958, **35** (8), 403–404.—In the semi-micro procedure described, a soluble chelating agent, *e.g.*, Na citrate, is used for Cu^{2+}. Subsequent reduction in hot alkaline soln. by an aldose gives insol. red cuprous oxide which is removed by centrifuging. The Cd^{2+} then left in soln. are identified as the sulphide by means of thioacetamide. O. M. WHITTON

2042. **2-Mercaptoquinoline (thiocarbostyril) as an analytical reagent for copper and palladium.** J. Xavier (Dept. of Inorg. Chem., Indian Assoc. for Cultiv. of Sci., Calcutta). *Z. anal. Chem.*, 1958, **163** (3), 182–187 (in English).—2-Mercaptoquinoline (**I**) in acetic acid or ethanol soln. is a highly sensitive and fairly specific reagent for the detection of Cu in HCl soln. On a test paper impregnated with a 0·2% soln. of **I**, the limit of identification is 0·03 μg of Cu at a dilution of 1 in $4{\cdot}3 \times 10^5$, and on a spot-plate with a 0·1% soln. of **I**, 0·025 μg of Cu at a dilution of 1 in 1×10^6. For the detection of Cu, Pd and Bi in the presence of each other, a disc-chromatographic method is recommended, the rings due to the cations being revealed by spraying with a 0·2% ethanolic soln. of **I**. In a spectrophotometric determination of Pd, a 0·1% soln. of **I** in 95% ethanol at a pH of 1·4 to 2·8 is used, the extinction being measured at 450 mμ. The sensitivity is 0·009 μg of Pd per ml. Interference is shown by Cu, Bi, Au, Hg^{I}, Hg^{II}, Fe^{III} and VO_3^{-}, whilst large amounts of Ni, Cr, W and Mo must be absent. This method is unsatisfactory for the determination of Cu. J. H. WATON

2043. **Polarographic determination of arsenic and tellurium in copper.** K. J. Cathro (C.S.I.R.O., Melbourne, Australia). *Aust. J. Appl. Sci.*, 1958, **9** (3), 255–264.—In the determination of 0·02 to 1 mg of As in a sample of cathode copper or copper leach soln., elementary As is pptd. with H_3PO_2 in 6 *N* HCl at 85° and is then dissolved in conc. HNO_3. After removal of HNO_3 by fuming with H_2SO_4 and reduction of As to the tervalent state with hydrazine sulphate, the soln. (adjusted to *N* H_2SO_4) is polarographed between − 0·2 and − 1·0 V. The concn. of As ($0{\cdot}5 \times 10^{-4}$ to $0{\cdot}5 \times 10^{-3}$ *M*) is proportional to the diffusion current. Tellurium interferes and, especially if the As : Te ratio is < 20, should be separated (after double pptn. of As plus Te from the Cu with H_3PO_2 and their dissolution in HNO_3) by selective pptn. with H_3PO_2 in H_2SO_4 soln. at 95° (As^{3+} should be present, and also $HgCl_2$ to replace Cu as catalyst during the reduction). The filtrate is polarographed for As, whilst the ppt. of Te is dissolved in HNO_3 and the soln., adjusted to pH 8 with aq. NH_3, is polarographed between − 0·3 and − 0·9 V ($E_{\frac{1}{4}}$ = − 0·6 V *vs.* the S.C.E.). The lower limit of determination is 0·05 mg of Te. The error is ± 3% for 0·1 to 1·0 mg of As alone, and ± 5% for As plus Te when both are present, although 0·25 mg of As is the lower limit of determination in this instance. W. J. BAKER

2044. **2-Mercapto- and 2-methyl-benziminazoles as reagents for silver.** R. L. Dutta (Inorg. Chem. Lab., Indian Assoc. for the Cultivation of Sci., Calcutta). *J. Indian Chem. Soc.*, 1958, **35** (8), 562–564.—These reagents are suitable for the rapid gravimetric determination of Ag in ammoniacal medium. After being dried at 120°, the silver salts have the compositions $C_7H_5N_2SAg$ and $C_8H_7N_2Ag$, respectively, and are stable towards light and heat. The interfering effects due to Cu, Ni, Co, Mn, Zn, Cd, Pb, Bi and Th are eliminated by masking with EDTA; Hg interferes. Potassium sodium tartrate is used to keep metals such as Al, Be and U in soln. I. JONES

2045. **Determination of silver, bismuth and lead in materials for silvering ceramics.** L. Plocek (Res. Inst. Electrotechn. Ceramics, Hradec Králové, Czechoslovakia). *Sklář a Keramik*, 1958, **8** (9), 182.—*Procedure*—The sample is homogenised and weighed quickly into a porcelain crucible containing filter-paper, dried and then ignited at 800°. *Silver*—The ignited sample (1 g) is dissolved in HNO_3 (1 : 3) (3 to 5 ml for 0·1 g of Ag), diluted to 250 ml, and to a 50-ml aliquot are added *M* ammonium acetate (50 ml), EDTA (disodium salt) (**I**) (2 to 3 g) (to mask interfering elements), water to 400 ml and aq. NH_3 till the mixture is alkaline to phenolphthalein. The mixture is heated and Ag is pptd. with mercaptophenylthiothiadiazolone (bismuthon) soln. (2·5%) (20 ml for 0·1 g of Ag). The ppt. is dried at 105° and weighed. *Bi_2O_3*—The ignited sample (1·5 g containing about 4% of Bi_2O_3) is dissolved in HNO_3 (1 : 3) and diluted with H_2O to 500 ml. The pH is adjusted to 2 to 4 and the soln. is titrated with 0·01 *M* **I** till yellow to catechol violet. *PbO*—The ignited sample is dissolved as described above, tartaric acid (5%) (2 ml) is added, and aq. NH_3 in excess, then KCN soln. (5%) (40 ml) and buffer soln. at pH 10 (NH_4Cl + aq. NH_3) (70 ml). The soln. is heated to 40° and titrated with **I**, with Eriochrome black T as indicator. J. ZÝKA

2046. **A new colorimetric method for the determination of beryllium with neo-thorin [arsenazo].** Shozo Shibata, Fukuo Takeuchi and Teiichi Matsumae (Gov. Ind. Res. Inst., Kita-Ku, Nagoya, Japan). *Bull. Chem. Soc. Japan*, 1958, **31** (7), 888–889 (in English).—Microgram amounts of Be can be determined by measuring the extinction of the stable violet complex with arsenazo in aq. soln. at either 570 mμ and pH 6 (for 0·15 to 1 p.p.m. of Be) or 580 mμ and pH 11·3 (for < 0·15 p.p.m.). The sensitivity in the first instance is 0·03 μg and in the second it is 0·002 μg. W. J. BAKER

2047. **Micro-determination of beryllium using ammonium aurintricarboxylate [aluminon] as a colorimetric reagent.** Anil K. Mukherji and Arun K. Dey (Chem. School, Univ. of Allahabad, India). *Chim. Anal.*, 1958, **40** (8), 299–303.—Previous work on the use of aluminon (**I**) as a colorimetric reagent for metals (*Anal. Abstr.*, 1957, **4**, 784) has been extended. Beryllium can be determined by means of its complex which has an absorption max. at 530 mμ. The soln. containing the beryllium as the chloride, nitrate or sulphate, at pH 6·0 ± 0·2 and at 20° to 30° is treated with a 50-fold excess of a freshly prepared aq. soln. of **I**. After 15 min. the optical density is measured at 530 mμ, with a spectrophotometer or a photocolorimeter. Beer's law is obeyed over the range 0·5 to 100 p.p.m. of Be. A comprehensive list of interfering ions is given with the max. permissible concn. in the sample soln. W. T. CARTER

2048. **Colorimetric determination of a trace of magnesium by the xylidyl blue method.** Hideo Ogata and Ko Hiroi (Central Res. Inst., Japan Monopoly Co-op., Shinagawa-ku, Tokyo). *Japan Analyst*, 1958, **7** (8), 483–487.—Mann and Yoe's determination of Mg with xylidyl blue [3-hydroxy-4 - (2 - hydroxy - 5 - sodium - sulphophenylazo) - 2 - naphtho-2′:4′-xylidide] (**I**) (*cf. Anal. Abstr.*, 1956, **3**, 2009) was examined with reference to the interference of Ca and a large amount of Na. Positive and negative errors are caused by Na and Ca, respectively; the errors, however, remain constant in the presence of > 400 p.p.m. of Na and > 5 p.p.m. of Ca, and the effects compensate each other. Sea water, or brine, from which most Mg is removed (remaining Mg < 0·4 p.p.m.), is made pH 7 to 8, mixed with **I** in 95% ethanol (0·15 mg per ml) (10 ml) and borax buffer at pH 9 (0·08 *M*) (1 ml). The amount of Na and Ca is adjusted as mentioned above, the vol. made up to 50 ml with 95% ethanol and the product is submitted to photometry at 510 mμ. The standard deviation is ≃ ± 4%. K. SAITO

2049. **Rapid method for the determination of calcium and magnesium oxides in basic refractory materials.** P. I. Protsenko. *Ogneupory*, 1958, (3), 138–139; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,697.—Complexometric determinations of Ca and Mg are used in the analysis of basic refractories. To 0·2 g of thoroughly ground sample in a platinum crucible add 10 g of $K_2S_2O_7$ and fuse for 15 to 20 min. at 700° to 800°. Cool, dissolve the melt by boiling with 50 to 60 ml of HCl (1:1), add 25% aq. NH_3 soln. to precipitate hydroxides and add a little in excess, stir, cool, dilute to 200 ml, stir and filter into a dry flask. To 20 ml of the resulting soln. (or 10 ml for a sample containing > 50% of MgO) add water (20 ml), buffer soln. (20 g of NH_4Cl and 90 ml of conc. aq. NH_3 soln. per litre) (30 to 50 ml), a 10% soln. of Na_2S (1 ml), a 5% soln. of hydroxylamine hydrochloride (1 to 2 ml) and 6 to 10 drops of Eriochrome black T (0·25 g of indicator dissolved in 5 ml of buffer soln. and diluted to 50 ml with ethanol), stir, and titrate total Ca plus Mg with 0·02 *M* EDTA (disodium salt). To another portion of the soln. add water (50 ml), 20% NaOH soln. (10 ml) and 0·1 g of indicator (0·1 g of murexide ground with 10 g of NaCl), stir and titrate with EDTA (disodium salt) to determine Ca. Determine Mg by difference. The analysis takes 45 to 60 min. In the absence of murexide, Ca may be titrated with oxalate. C. D. KOPKIN

2050. **Recent progress in the complexometric determination of calcium and magnesium in slags.** V. Kuhn (Centre Tech., Ind. de la Fonderie). *Chim. Anal.*, 1958, **40** (9), 340–344.—The indicator Calcon (C.I. 202) (here called Blue Black Chrome RF) recommended by Hildebrand and Reilley (*Anal. Abstr.*, 1957, **4**, 2518) is preferred to that of Patton and Reeder (*Anal. Abstr.*, 1956, **3**, 2912). Re-acidification followed by ammoniacal buffering permits determination of Mg in the same soln., with Eriochrome black T as indicator; optimum pH values are discussed. Iron and Al are removed by $CHCl_3$ extraction of their acetylacetonates or cupferronates and Mn by extraction with Na diethyldithiocarbamate at pH 4 to 5. P. D. PARR-RICHARD

2051. **The complexometric titration of calcium in the presence of magnesium. A critical study.** R. Belcher, R. A. Close and T. S. West (Dept. of Chem., The Univ., Birmingham, England). *Talanta*, 1958, **1** (3), 238–244.—Several indicators were tested for this titration (with 0·01 *M* EDTA). Murexide gives really sharp end-points only when Mg is absent; the same is true for calcein. When the ratio of Mg:Ca is < 1:5, a good end-point is given by methyl thymol blue and the recovery of Ca is quant., but for ratios of Mg:Ca of ≃ 1:1 the indicator fails. Calcon gives true results only in the presence of Mg (1:10 to 1:5 of Mg to Ca). For higher amounts of Mg, premature end-points appear, but revert in 2 to 3 sec. In the absence of Mg or for ratios of < 1:12, a sharp red to blue end-point is obtained with Acid alizarin black SN; for larger amounts of Mg, the recovery of Ca is low. If EDTA is replaced by 1:2-diaminopropane-NN′-tetra-acetic acid, a Mg:Ca ratio of 1:5 is possible with this indicator. All indicators except Calcon were used as solid dispersions in appropriate salts. Buffers recommended are NaOH or KOH for calcein, and diethylamine for Calcon, murexide and alizarin black; either is suitable for methyl thymol blue. P. D. PARR-RICHARD

2052. **The determination of strontium and barium by paper chromatography.** F. Modreanu (Inst. Chim. "Petru Poni," Acad. R.P.R., Iaşi, Romania). *Naturwissenschaften*, 1958, **45** (13), 310.—The barium and strontium salts are chromatographed as the propionates, which are prepared by dissolving the carbonates in the acid or by passage through a column of ion-exchange resin which is in the propionate form (*e.g.*, Amberlite IRA-400). Standard mixtures of the salts with Sr:Ba ratios varying from 9:1 to 2:8 are prepared from 0·1 *M* soln. The chromatograms are developed on Whatman No. 1 paper with ethanol - water - propionic acid - aq. NH_3 (20:2:1:1) in equilibrated tanks for 6 hr. at 20°. They are then dried at 60° for 0·5 hr. The spots are revealed by spraying with a freshly prepared saturated soln. of sodium rhodizonate. For quant. evaluation, the spot size is determined by planimetry. A calibration curve is essential as there is no linear relationship between spot size and concn. E. KAWERAU

2053. **Detection of zinc in ores by a grinding method.** E. P. Ozhigov. *Soobshch. Dal'nevost. Fil. Akad. Nauk SSSR*, 1958, (9), 127–129; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,225.—Copper tetrathiocyanatomercurate (**I**), already proposed for the detection of Zn in minerals by a grinding method (*Ref. Zhur., Khim.*, 1955, Abstr. No. 55,417), is used for the detection of Zn in ores of

various composition. To 5 to 10 mg of the ground sample add 3 or 4 times the amount of a mixture of NH_4Cl and NH_4NO_3, mix, heat until yellow, cool, add a little **I** and a drop of H_2SO_4 (1:1). In the presence of Zn, a lilac or dark-lilac colour appears at the spot where the acid is added. The intensity of the colour is directly proportional to the content of Zn. The sensitivity of the reaction is $\simeq$ 0·2%; the detectable minimum is $\simeq$ 0·2 mg of Zn.

C. D. KOPKIN

2054. **Determination of zinc by the use of resorcinol.** Kh. L. Arvan. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 198–203; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,226.—The change of light absorption of soln. of resorcinol in ammoniacal and in acid media is used in the determination of Zn^{2+} (0·1 to 2·0 mg per ml). In ammoniacal media, increase of concn. of Zn^{2+} leads to an increase in the absorption in the region 600 to 620 mμ. The colour is not completely developed, so that this method cannot be used for the determination of Zn^{2+}. On acidification of the ammoniacal soln., absorption at 480 mμ is observed and the increase in the total absorption ceases; however, the intensity of the latter depends on the constitution of the ammoniacal soln. which is acidified. It is not always possible to stop the process even in rigorously controlled soln. The presence of Zn^{2+} greatly influences the change of the absorption spectra of resorcinol in HCl soln. (the absorption bands at 520 and 665 mμ are greatly strengthened; in the absence of Zn^{2+} they are only just noticeable). The increase in the general absorption and the re-distribution of the max. are accelerated on warming. The colour may be stabilised by dilution, with water, of the previously heated intensely coloured acid soln., but even minor modifications in the conditions lead to poor reproducibility.

C. D. KOPKIN

2055. **Rapid analytical method for zinc fluorosilicate.** M. Man. *Rev. Chim., Bucharest*, 1958, **9** (7–8), 466–467.—The method is based on the reaction of Zn^{2+} with $K_4Fe(CN)_6$ which furnishes K^+ for the pptn. of K_4SiF_6, the determination being in three phases—total fluorine content, free fluoride content, and SiF_6^{2-} content. *Procedure*—The sample (2·5 g) is dissolved in 250 ml of water and filtered, and silica is determined by the usual method. A 10-ml aliquot of the filtrate ($\simeq$ 0·04 to 0·05 g of $ZnSiF_6$) is diluted with 50 ml of water and titrated with NaOH (10 *N*) with phenolphthalein as indicator until the red colour is not intensified with one drop further (*a* ml)—(this is to ensure a true end-point since hydrolysis of NaF can occur if the sample contains 30 to 40% of $ZnCl_2$). Another 10 ml of the filtrate is treated with 5 ml of a saturated soln. of $K_4Fe(CN)_6$; the flask is cooled with ice and the contents are titrated with NaOH (10 *N*), with phenolphthalein as indicator, until pink (*b* ml). (The flask must be waxed and the water used boiled free from CO_2 and chilled.) The contents are then diluted with a further 250 ml of the CO_2-free water and titration is continued slowly at room temp. until the pink colour persists for 2 min. (*c* ml). Then $ZnSiF_6.6H_2O$ (%) = $(7{\cdot}886c \times 25)/d$, where *d* is the wt. of the substance used; and ZnF_2 (%) = $[5{\cdot}169a - (1{\cdot}5c + b)] \times 25/d$; and HF (%) = $(2b \times 25)/d$.

H. SHER

2056. **Effect of supporting electrolyte on polarographic reduction of *p*-benzoquinone.** J. W. Collat (State Univ., Columbus 10, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1726–1729.—In the reduction of *p*-benzoquinone at the dropping-mercury electrode, soln. containing Mg^{2+} and Zn^{2+} behave like buffers in controlling the pH at the surface of the drop because of the formation of an insoluble hydroxide. When the concn. of the cation is known, the solubility product of the hydroxide can be estimated from the current-potential data. Several modifications of zinc hydroxide have been examined in this way.

K. A. PROCTOR

2057. **Separation of zinc from nickel in ammoniacal solution with thioacetamide.** L. Bloch (Lab. H. J. van der Rijn N.V., Naarden, Netherlands). *Chem. Weekbl.*, 1958, **54** (29), 384–386.—Remove the Fe^{3+} with aq. NH_3 after addition of an ammonium salt. Warm the soln. with an excess of thioacetamide until the white ZnS ppt. changes to grey, cool immediately, filter and wash rapidly with 3% $(NH_4)_2SO_4$ soln. Pptn. takes place gradually. At about 70° the nickel starts pptg. but an excess of HCl in the filtrate prevents this. For the detection of Zn in nickel-copper alloys, first precipitate Cu with thioacetamide and filter. Boil the filtrate until H_2S-free, cool, make ammoniacal and warm with thioacetamide. A white ppt. indicates Zn.

P. RENTENAAR

2058. **Polarographic determination of zinc in the presence of a large amount of nickel and cobalt.** Shigeru Yokosuka and Fumiki Morikawa (Bessi Mine Office, Niihama, Ehime-ken). *Japan Analyst*, 1958, **7** (8), 512–514.—In NaOH soln. > 1·5 *N*, Zn gives a distinctive wave in the presence of EDTA at $-$ 1·2 V *vs.* the S.C.E.; Co and Ni are masked under these conditions. The wave height is proportional to concn. for 0·1 to 10 mg per 100 ml. A sample (containing 500 mg of Ni) of an electrolytic soln. for the production of Ni is boiled with NH_4Cl (3 g) and aq. NH_3 soln. (sp. gr. 0·90) (20 ml), filtered, mixed with EDTA (disodium salt) (5 g) and NaOH (10 *N*) (20 ml), made up to 100 ml and submitted to polarography. No interference results from < 500 mg of Ni and < 10 mg of Co.

K. SAITO

2059. **The polarographic determination of copper, bismuth and lead in high-purity zinc by the use of EDTA.** K. Győrbíró, R. Szegedi and I. Miklós (Dept. Inorg. Chem., Technol. Univ., Budapest). *Magyar Kém. Foly.*, 1958, **64** (9), 348–351.—The polarographic separation of ter- and bi-valent cations can be achieved even if both cations form complexes with EDTA. The optimum pH is 1. *Procedure*—For the determination of Bi in zinc in the presence of Cu and Pb, dissolve the metal (5 to 20 g) in dil. HNO_3 and, if necessary, evaporate off part of the excess acid. Adjust the pH to $\simeq$ 1 with aq. NH_3. Add gelatin soln. (a few drops) and dilute to 25 or 50 ml. To an aliquot of 5 ml add water (2 ml), remove the oxygen by passing N through the soln., and polarograph. Copper and Bi give a composite wave, but that of Pb is separate. To a second 5-ml aliquot add 0·15 *M* EDTA (disodium salt) (2 ml), remove the oxygen and polarograph at pH $\simeq$ 1. Any ppt. formed does not interfere. Copper gives a separate wave, but those of Pb and Bi are combined. From this last wave the height of the previous wave due to Pb is subtracted; the difference gives the height due to Bi. The evaluation of the wave is best carried out by the addition method. In the presence of a 10-fold excess of Pb, 0·002% of Bi can be determined.

A. G. PETO

2060. **Ion-exchange separation of zinc, cadmium and mercury in aqueous and partial non-aqueous media.** E. W. Berg and J. T. Truemper (Coates Chem. Lab., State Univ., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1827–1830.—Zinc, Cd and Hg can be separated quant. as their chloro complexes, in 0·01 *M* HCl, on an anion-exchange resin (Dowex 1, Cl form, −60 + 100 mesh). Zinc and Cd are eluted in succession, each with 0·01 *M* HCl (preferably containing methanol), and then Hg with 0·01 *M* HCl - 0·1 *M* thiourea. Recoveries are nearly always complete; no regeneration of the resin is necessary. The separation (60-ml sample) can be made by elution with aq. 0·01 *M* HCl (28-cm column), 0·01 *M* HCl - 10% (v/v) methanol (18-cm column) or 0·01 *M* HCl - 25% (v/v) methanol (6-cm column), with a flow rate of 1·5 to 2 ml per min. in each instance.

W. J. BAKER

2061. **Determination of cadmium in zinc concentrates and other zinc-rich materials. Anion-exchange procedure.** S. Kallmann, H. Oberthin and R. Liu (Ledoux & Co., Teaneck, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1846–1848.—After dissolution of the sample (1 to 5 g) and removal of Pb as $PbSO_4$ and Cu by deposition on iron, Cd can be separated from Zn by formation of the stable CdI_4^{2-} complex in 0·75 *N* H_2SO_4 containing 5% (w/v) of KI, followed by retention of this complex on Dowex-1 resin, the Zn and other elements passing through quant. A column (12 in. × 1 in.) containing a settled bed of resin (2 in. deep, 200 to 400 mesh) is used, approx. 600 ml of iodide reagent being required to elute 3 g of Zn. The resin is then washed with 0·1 *N* HCl and the CdI_4^{2-} are eluted with 3 *N* HNO_3. Procedures are given for determining Cd in the eluate by dithizone (for < 5 μg), polarography (0·1 to 50 mg), EDTA titration (for 1 to 500 mg) and electrolysis (for > 10 mg). The accuracy is high for contents of Cd from 0·004 to 16%. The preliminary removal of Pb and Cu also ensures the quant. removal of Ag, Au, Bi, As and Sb, which either form insol. iodides or are partly adsorbed by the resin.

W. J. BAKER

2062. **A new rapid method for the gravimetric determination of cadmium.** J. Dick and J. Ristici (Inst. Politeh., Timişoara, Romania). *Acad. R.P.R., Baza Cercet. Ştiinţ. Timişoara, Stud. Cercet. Ştiinţ., Ser. I*, 1957, **4**, 55–59.—Amidopyrine forms complexes with complex metal ammino anions, the amidopyrine occupying two co-ordinating positions. Co-ordination to the central metal atom takes place through the methylated N atoms. The cadmium thiocyanate complex with amidopyrine is one of the most stable and insoluble. The ppt. obtained has the formula $Cd(C_{13}H_{17}ON_2)_2(SCN)_2$, and is white, stable at 110°, and soluble in hot water and mineral acids. The concn. limit of the test is 10 μg of Cd^{2+} per ml; Sn, Cu, Co, Ni, Ag, Pb, Zn and Hg must be absent.

CHEM. ABSTR.

2063. **Determination of small amounts of mercury in inorganic raw materials.** E. Kroužek and P. Povondra (Res. Inst. of Ores, Prague). *Chem. Listy*, 1958, **52** (9), 1825–1827.—Mercury in ores is separated by distillation as chloride. *Procedure*—Dissolve the finely powdered sample containing 0·2 to 20 mg of Hg either with a mixture of HCl and HNO_3, in the cold (for sulphide ores), or by heating with HCl and oxidising with HNO_3 (iron ores). Transfer the soln. with any undissolved residue by means of a small vol. of H_2O into a 100-ml distillation flask, add dilute H_2SO_4 (1 : 1) and distil till fumes of SO_3 appear. Then add, while heating, dil. HCl (1 : 1) (25 ml) dropwise from a separating funnel; 50 mg of Hg can be distilled in 100 min. For larger amounts of Hg the vol. of acid and the time of distillation must be increased. The Hg in the distillate can be determined by known methods. Small amounts of Fe and Sb are distilled together with the Hg, but cause no interference.

J. ZÝKA

2064. **Study of neutron absorptiometry and its application to the determination of boron.** D. D. DeFord and R. S. Braman (Dept. of Chem., Northwestern Univ., Evanston, Ill.). *Anal. Chem.*, 1958, **30** (11), 1765–1772.—Thermal neutron absorption may be used advantageously for the determination of B with its high neutron absorption cross-section. The sensitivity, accuracy and selectivity depend largely on the geometrical arrangement of source, sample and detector, and are greatest when the detector is completely surrounded by sample and when both source and sample are embedded in the paraffin moderator. This permits the use of small (10-mC) sources and short (10-min.) counting times. The range of B concn. in the sample solution (25 to 225 ml) is 0·01 to 4·0 g-atoms per litre; counting rate is related to B concn. by a simple equation. Best results (accuracy to within ± 0·5%) are obtained on about 1 g of B; on 0·1 g the error is ± 2%. The method is rapid and the chemical state of the B immaterial; separation from other elements is unnecessary.

J. P. STERN

2065. **Periodate and iodate methods of analysis of elementary boron and borides.** L. Ya. Markovskiĭ and G. V. Kaputovskaya (State Inst. of Appl. Chem.). *Zavod. Lab.*, 1958, **24** (9), 1065–1066.—The sample (0·02 g) of B or boride is boiled under reflux with a soln. (vol. not stated) containing 0·5 g of KIO_4 or KIO_3 and 1 ml of conc. HNO_3 or HCl until decomposed. The cooled soln. is mixed with 4 to 5 ml of 0·1 *N* HCl or HNO_3 and 0·1 g of KI, and the liberated iodine is just destroyed by addition of $Na_2S_2O_3$ soln. The operations, addition of KI, etc., are repeated until no more iodine is liberated. The excess of mineral acid is then destroyed by addition of KIO_3 and KI and titration of the iodine with 0·1 *N* $Na_2S_2O_3$, and these operations are also repeated until no more iodine is liberated on addition of KIO_3 and KI. The colourless soln. is then titrated in the presence of mannitol with 0·1 *N* $Ba(OH)_2$ to give the content of B_2O_3. The complete determination takes 1·5 hr. With materials not completely decomposed in the initial attack, *e.g.*, MgB_{12}, the insol. matter is treated separately. It is fused with Na_2CO_3 and K_2CO_3, the melt is boiled with HCl under reflux for 30 min. (to remove CO_2), the acid in the cooled soln. is destroyed as described above, and the B_2O_3 is titrated with $Ba(OH)_2$ in the presence of mannitol.

G. S. SMITH

2066. **Determination of fluoroborates in iron, nickel and copper electrolytes.** E. I. Lerman. *Sb. Trud. Vses. Nauch. Inst., Goznak*, 1957, (1), 243–249; *Ref. Zhur., Khim.*, 1958, (24), Abstr. No. 81,351.—Gravimetric and photometric methods are evolved for the determination of fluoroborates in iron, nickel and copper electrolytes. The gravimetric method is based on pptn. of fluoroborates with nitron. Dilute 25 ml of iron or nickel electrolyte (concn. of $HBF_4 \simeq 10$ g per litre) to 250 ml, and to

50 ml of the resulting soln. add, while cooling in ice, 10 ml of glacial acetic acid and, with stirring, 10 ml of a 10% soln. of nitron in 5% acetic acid. After setting aside the mixture for 2 hr. in ice, collect the ppt. in a No. 3 glass crucible, wash it with ice-water (10 to 15 ml) acidified with acetic acid, dry it at 105° to 110° and weigh. The conversion factor to HBF_4 is 0·2195. To determine fluoroborates in copper electrolytes, first precipitate Cu by adding $\simeq$ 1·7 g of reduced iron. The determination takes 5 to 6 hr., with an error of $<$ 6%. For the photometric determination, make 1 to 3 ml of electrolyte up to 500 ml, transfer 3 ml of the resulting soln. to a separating funnel, add water (20 ml), 2% soln. of Na_2SO_4 (5 drops), 0·1% soln. of methyl violet (10 drops) and benzene (10 ml), and shake for 3 min. After setting aside for 10 min., discard the aq. layer, and measure the extinction of the benzene layer with a green filter in 10-mm cells. The determination takes 20 to 25 min.; the error is up to 8%. C. D. KOPKIN

2067. **Complexometric titrations (chelatometry). XXXIX. Rapid determination of aluminium in ferrosilicon.** L. Brháček (VŽKG, Ostrava, Czechoslovakia). *Chem. Listy*, 1958, **52** (9), 1820–1822.—The total amount of Al plus Fe is determined by addition of excess of EDTA (disodium salt), and back-titration of the excess; Fe is determined by a direct complexometric titration, with salicylic acid as indicator. When determining Al in ferrosilicon, the excess of Fe must be removed by electrolysis with a mercury cathode. J. ZÝKA

2068. **A rapid simultaneous photometric determination of aluminium and iron in titanium or vanadium by extraction with oxine.** Hiroshi Hashitani and Kenji Motojima (Japan Atomic Energy Res. Inst., Tokai, Ibaragiken). *Japan Analyst*, 1958, **7** (8), 478–483.—Since Ti ($<$ 20 mg of TiO_2) and V ($<$ 200 mg of V_2O_5) are masked by H_2O_2 in an ammoniacal soln., Al (5 to 100 μg of Al_2O_3) and Fe (5 to 150 μg of Fe_2O_3) are extracted with $CHCl_3$ in the form of an 8-hydroxyquinoline (**I**) complex and determined photometrically at 390 and 470 mμ (*cf. Anal. Abstr.*, 1956, **3**, 1725). A weakly acid soln. is treated with H_2O_2 (30%) (3 ml) and **I** (1%)(3 ml) in acetic acid and the pH is adjusted with dil. aq. NH_3 soln. (8·0 to 10·7 and 4·5 to 10·7 in the presence of Ti and V, respectively.) The mixture is diluted to 100 ml and extracted with $CHCl_3$ (10 ml); the organic layer is dried with Na_2SO_4 (1 g) and submitted to photometry. Copper and Ni ($<$ 1 mg each) are back-extracted from the $CHCl_3$ soln. with KCN soln. of pH 8·5 to 9·0. Manganese is back-extracted with ammonium acetate soln. of pH 5 from the $CHCl_3$ soln. washed with an ammonium buffer of pH 8·5. No interference results from Cr ($<$ 2·5 mg) and P ($<$ 3 mg), provided that the extractions are carried out at pH $>$ 10 and $>$ 8, respectively. K. SAITO

2069. **Determination of aluminium in the presence of titanium by Chirkov's method.** A. Kocharyan. *Sb. Student. Nauch. Trud. Erevansk. Univ.*, 1958, (8), 197–203; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,233.—Titanium interferes with the electrometric determination of Al by Chirkov's method [*cf. Zavod. Lab.*, 1948, (7)] because of the formation of the fluoride complex TiF_6^{2-}. The interference cannot be eliminated by increasing the pH of the soln. since, because of the extremely high stability of the complex, the reaction—

$$Ti(OH)_4 + 6F^- = TiF_6^{2-} + 4OH^-$$

takes place. However, Ti^{3+}, as distinct from Ti^{4+}, do not react with F^- in an acetic acid medium. On this basis, an electrometric determination of Al with F^- in an acetic acid medium, after reduction of Ti^{4+} with zinc amalgam, is evolved. C. D. KOPKIN

2070. **Neutron-activation analysis of aluminium-base alloys.** W. A. Brooksbank, jun., G. W. Leddicotte and J. A. Dean (Oak Ridge Nat. Lab., Tennessee, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1785–1788.—The precision of comparative neutron-activation analyses of Cu, Mn, Ni, Zn, Fe and Ti in aluminium matrices is examined, results being compared with average certificated analyses. For major components, the accuracy is generally within $\pm$ 5 to 7%. The method is adequate for Mn, Fe and Ti; after removal of Si it has a positive bias only for samples high in Cu, and a negative bias for some Zn-containing samples. The presence of ^{31}Si in ^{65}Ni is revealed by γ- but not by β-counting. Among trace constituents (0·0001 to 0·05%), Co, Sb, Ag and Zr are also determined, but results are not verified. The method does not replace conventional methods except when minute samples only are available. J. P. STERN

2071. **New fluorescent indicators. III. Volumetric determination of aluminium and zinc in alloys.** Z. Holzbecher (Inst. Anal. Chem., High School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (9), 1822–1825.—Analytical application of the previous study (*Anal. Abstr.*, 1959, **6**, 77) is described. *Aluminium and zinc in copper alloys*—Dissolve the sample (0·17 to 1·30 g for 40 to 5% of Zn, 0·07 to 0·54 g for 40 to 5% of Al) in HNO_3 (1 : 1), evaporate to dryness, moisten with a few drops of conc. HNO_3 and dissolve in H_2O (50 ml). Filter off SnO_2, wash with hot dil. HNO_3 (0·5%), add to the filtrate conc. HNO_3 (8 ml) and remove the excess of Cu and small amounts of Pb by electrolysis till the soln. becomes colourless. Evaporate to dryness, moisten with a few drops of acetic acid, dissolve in H_2O (10 ml), add *M* acetate buffer soln. at pH 5·1 (10 ml), $Na_2S_2O_3$ soln. (20%) (2 to 10 ml), and an ethanolic soln. of *o*-salicylideneaminophenol (0·05%) (2 ml) as indicator and titrate the Al in u.v. light with 0·6 *M* NaF till the yellow-green fluorescence disappears. Add 0·6 *M* NaF in excess (1 ml) and an ethanolic soln. of salicylaldehyde acetylhydrazone (0·1%) (2 ml) and titrate the Zn with 0·1 *M* EDTA (disodium salt) until the blue fluorescence disappears. *Aluminium in zinc alloys*—Dissolve the sample in dilute HCl, add a few ml of conc. HNO_3 and evaporate to dryness. Moisten with glacial acetic acid (1 to 2 drops) and dissolve in H_2O (5 to 10 ml). Add acetate buffer soln. (pH 5·1) (10 ml), $Na_2S_2O_3$ soln. (20%) (2 to 5 ml) and indicator soln. (2 ml) and titrate with 0·6 *M* NaF. *Aluminium and zinc in magnesium alloys*—For Zn, dissolve the sample in dil. HNO_3, add H_2SO_4 and evaporate to white fumes. Separate SiO_2 and precipitate Zn and Cu as sulphides in slightly acid soln. Dissolve ZnS in HCl and a few drops of HNO_3, evaporate to dryness, moisten with acetic acid, dilute with H_2O (5 to 10 ml), add acetate buffer soln., $Na_2S_2O_3$ soln. (20%) (2 to 5 ml) and NaF soln. (4%) (2 to 5 ml), and titrate the Zn as before. For Al, dissolve the sample as before, separate SiO_2 and isolate Al with Fe by addition of hexamine; wash the ppt. with hot NH_4Cl soln. (5%), dissolve in HCl, evaporate to dryness, and continue as described above. J. ZÝKA

2072. **New colorimetric method for the determination of small amounts of thallium.** G. G. Shchemeleva. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 135–140; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,239.—The method is based on extraction with toluene of the product of the reaction between $TlCl_4^-$ and methyl violet (**I**), with subsequent colorimetry or photometry of the resulting extract (the max. absorption of the coloured soln. is at 574 mμ; the mol. extinction coeff. is 50,000; the colour is stable for 16 to 20 hr.). For the visual determination of Tl^{3+}, to 1 to 3 ml of soln. add *N* HCl (0·7 ml) and a 0·02% soln. of **I**, dilute to 5 ml, extract with toluene (5 ml) and compare the colour of the organic layer with that of standard soln. containing known amounts of Tl. For photometry, the optimum conditions are 1 ml of *N* HCl and 2·8 ml of a 0·01% soln. of **I** in 10 ml of final soln. Beer's law is obeyed in the concn. range 0·1 to 2·5 μg of Tl per ml of soln., with toluene as comparison soln. Remove Sb, Bi and Sn before the determination. The methods have been tested on soln. of pure salts, artificial mixtures and industrial samples of metallic cadmium and lead. The max. relative error of the determination is ≯ 3%. C. D. Kopkin

2073. **Chemical studies on radioactive indicators. XIX. Separation of yttrium from an equilibrium mixture by mercury-cathode electrolysis.** Masayoshi Ishibashi, Taitiro Fujinaga and Atsuyoshi Saito (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 978–980.—Hildebrand's double-cylinder cell was employed for the electrolytic separation of ^{90}Y from ^{90}Sr in radiochemical equilibrium. When a dil. HCl soln. of the sample is electrolysed with a mercury cathode and a silver anode with a d.c. current of 10 V for 2 hr., almost all of the ^{90}Sr is removed, carrier-free ^{90}Y remaining in the inner cell. The time taken for complete separation is decreased by the addition of carrier to ^{90}Sr. K. Saito

2074. **Determination of rare-earth metals in their mixtures.** A. Almásy (Res. Inst. of the Heavy Metal Indust., Veszprém, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (1), 55–67 (in English).—The stepwise elution of rare earths from a column of Dowex-50 resin was found to be preferable to the gradient elution of Nevik (*cf. Anal. Abstr.*, 1956, **3**, 1284). The eluents are prepared by removing inorganic cations from lactic acid with Dowex-50 resin, and diluting it to molar concn. with aq. phenol soln., so that the mixture is 0·1 *M* with respect to phenol. A portion of this is treated with aq. NH_3, and used to adjust the pH of the eluents used. For the determination, the mixed rare-earth oxides (≯ 0·2 g) are dissolved in HCl, most of the HCl is removed by evaporation, the soln. sealed in an ampoule, and exposed to a neutron flux sufficient to give a measurable degree of activity to all rare-earth metals present. The soln. is then adsorbed on a small column of Dowex 50. The resin is washed till the eluate is neutral, and then transferred to a column which is in equilibrium with the first of the series of eluents. Elution is then commenced with the first eluent at 76°, at a pressure giving a flow rate of 5 cm per min., the eluate being continuously scanned by a Geiger - Müller counter, and receiving flasks being changed when a rise or fall in activity is observed. Suitable apparatus is illustrated. When a metal appears in the receiving flask, the eluent is changed for the one of next higher pH, and so on. Each metal is thus obtained in one or more flasks. These are examined spectroscopically for rare-earth metal, and, if this is indicated, it is determined by pptn. with oxalic acid and ignition. If preliminary tests do not suggest the use of another series, eluents of the following pH values are recommended, each pH being accurate to ± 0·01 at room temp.—3·00 (Sc, Lu, Yb); 3·05 (Tm, Er, Ho); 3·10 (Y, Dy, Tb); 3·15 (Gd, Eu); 3·25 (Sm, Pm); 3·30 (Nd, Pr); 3·44 (Ce); 3·50 (La). Recoveries of single metals ranged from 84 to 105%, and relative errors in the determination of six metals from synthetic mixtures ranged in one case from − 25% to + 1% (mean − 14%) and from − 19% to + 3% (mean − 6%) in another. Recovery as individual metals from 0·2083 g of an unknown mixture totalled 0·1929 g. The accuracy is comparable with that of the oxalate method, and it is suggested that the method is applicable to mixtures of the tervalent ions of actinides. R. E. Essery

2075. **Spectrophotometric determination of rare earths.** J. S. Fritz, M. J. Richard and W. J. Lane (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1776–1779.—Concn. of ≃ 10^{-4} to 10^{-5} *M* of Y, La, Pr, Nd, Sm, Dy, Er and Yb can be determined quant. by measuring the extinction at 570 mμ and pH 8 (triethanolamine buffer) of the coloured complex with arsenazo. The practical mol. extinction coeff. used are $\epsilon_c - \epsilon_r$ (c = complex, r = reagent); these (listed) range from 24·7 to 26·2 × 10^{-3}. Interference from Fe and other reducible metals should be obviated by electrolysis (mercury cathode), from Al by masking with sulphosalicylic acid, from U^{4+} (if > 100-fold excess) by extraction as the diethyldithiocarbamate, and from Mg or Ca by making the measurements at pH 5 (but with some loss of sensitivity). Thorium, Zr, Ti, F^- and PO_4^{3-} interfere seriously; if these are absent the method is rapid and selective. W. J. Baker

2076. **Determination of trace impurities in samarium and europium oxides.** A. Brukl and K. Rossmanith. *Monatsh. Chem.*, 1957, **88**, 569–577.—Standard mixtures of Sm_2O_3, Eu_2O_3 and Nd_2O_3 were subjected to spectrographic measurements with a Hilger spectrograph to determine how small quantities of each could be measured when present as impurities in the others. The method of Fassel was employed. A pair of spectral lines is chosen such that a weak line of the main element is used for reference, and a strong line of the contaminant is compared with it. The pairs of lines recommended are—(*i*) for Sm_2O_3 in Eu_2O_3, Sm 4424·35 A - Eu 4426·41 A, to a low limit of 0·005% of Sm_2O_3, with an average error of ± 9%; (*ii*) for Nd_2O_3 in Sm_2O_3, Nd 4305·57 A - Sm 4299·35 A, or Nd 4012·25 A - Sm 4011·72 A, to a low limit of 0·02% of Nd_2O_3, with an average error of ± 7·4%; (*iii*) for Eu_2O_3 in Sm_2O_3, either Eu 4129·73 A - Sm 4128·10 A, or Eu 3930·51 A - Sm 3931·16 A, or Eu 4129·73 A - Sm 4129·24 A, to low limits of 0·001%, 0·05% and 0·1% of Eu_2O_3, respectively. All have an average error of ± 7%. Chem. Abstr.

2077. **Determination of impurities in carbon dioxide by gas chromatography, with special reference to coolant gas for nuclear reactors.** D. G. Timms, H. J. Konrath and R. C. Chirnside (General Electric Co. Ltd., Wembley, England). *Analyst*, 1958, **83**, 600–609.—By the gas-chromatographic method described, H, A, O, N, CH_4 and CO present in

carbon dioxide in amounts as low as 5 to 20 p.p.m. can be determined with a 25-ml sample. A molecular sieve is used for the separation. The CO_2 is first removed by absorption in soda lime and only the dried impurity gases are carried into the zeolite column. Hydrogen and argon were used as carrier gases. When argon, which cannot be separated from O, is present in the sample, it can be determined by difference by use first of argon and then of hydrogen as the carrier gas, or the oxygen can first be removed by means of a catalyst (De-oxo). The detector consists of a sensitive katharometer combined with a recording millivoltmeter. The apparatus is described in detail. A. O. JONES

2078. **Direct determination of cyanides in zinc plating baths.** K. Lusk and B. Holenda (Tesla, Pardubice, Czechoslovakia). *Chem. Listy*, 1958, **52** (9), 1829.—Cyanides in plating baths can be directly titrated with a soln. of $NiSO_4$ with the use of dithio-oxamide as indicator; no previous separation of sulphides need be carried out. *Procedure*—To the sample (1 ml) add aq. NH_3 (1:1) (10 ml) and H_2O (50 ml) and titrate with a soln. of $NiSO_4$ (10 g of $NiSO_4.7H_2O$ in 1 litre), determining the end-point by a spot test on paper saturated with a 0·5% ethanolic soln. of dithio-oxamide. The titration is finished as soon as a red colour appears. J. ZÝKA

2079. **Determination of silica in silicates.** I. A. Voinovitch (Lab. Soc. Franç. Céram., Centre National d'Études et Recherches Céramiques). *Chim. Anal.*, 1958, **40** (9), 332–339.—Studies have been made of the scope, precision, reproducibility, specificity and rapidity of various methods for determining SiO_2 in silicates containing moderate amounts of SiO_2. A plastic clay ($SiO_2 \simeq 70\%$) was used for all determinations. Tables are given showing the max. deviations of different methods. Semi-micro methods using oxine or quinoline are satisfactory but require manipulative care. Pptn. of K_2SiF_6 and titration of HF formed by hydrolysis is rapid, simple, and wide in scope. Of colorimetric methods, those giving a blue SiO_2 - molybdate complex are to be preferred; spectrography is even more rapid. Treatment with HCl and gelatin to make the SiO_2 insol. is simple, reproducible and fairly rapid. *Procedure*—Fuse 0·5 to 1 g with 4 to 5 g of $KNaCO_3$ in a platinum crucible. Place the crucible and its cover in a beaker with 150 to 200 ml of hot water and 25 ml of conc. HCl. After dissolution is complete, wash the crucible and its cover with water and evaporate to dryness. Add 35 ml of conc. HCl and boil for 6 min. Add another 2 ml of HCl and 15 ml of water, followed by 10 to 12 ml of warm 3% aq. gelatin soln. Stir and leave for 5 min. then filter. Wash the ppt. 5 or 6 times with hot dil. HCl - gelatin soln, dry, ignite and weigh. Remove SiO_2 by evaporation with HF, ignite again and weigh. P. D. PARR-RICHARD

2080. **Spectrophotometric determination on filter-paper of germanium, phosphorus and arsenic.** J. M. O. Damon and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1849–1855.—The total colour of the yellow 12-molybdo anion spots of Ge, P and As separated chromatographically can be measured, $\simeq 1$ hr. after spraying the paper with ammonium paramolybdate in HNO_3, by a continuous scan at 375 mμ on a Cary recording spectrophotometer. A spray assembly and procedure for ensuring uniform application of molybdate reagent on to the filter-paper strips and maintenance of colour stability of the spots during drying are described. The relation between mean absorption-peak area and wt. of element is approx. linear for 0 to 10 μg of Ge. 0 to 3·5 μg of P and 0 to 10 μg of As, whilst the reproducibility is generally within 12% (range in area of mean area for triplicate peaks). The effect of other ions (SiO_3^{2-}, MoO_4^{2-}, WO_4^{2-}, $Cr_2O_7^{2-}$ and Fe^{3+}) and the conditions for minimum interference are established. In general, 5 μg of Ge can be determined satisfactorily in the presence of a 10-fold excess of P, As, V, Cr and Fe, and 2 μg of P in a 20-fold excess of Si, As and V or a 5-fold excess of Ge. Max. interference is associated with those ions (*i*) that have R_F values close to that of Ge, P or As, or which also produce a colour with the reagent or absorb between 350 and 400 mμ, and (*ii*) that form a complex with the element being determined, thus producing a second migrating species. W. J. BAKER

2081. **Detection of tin in ores by a grinding method.** E. P. Ozhigov. *Soobshch. Dal'nevost. Fil. Akad. Nauk SSSR*, 1958, (9), 129–130; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,244.—The detection of Sn with dimethylglyoxime by a grinding method (*Ref. Zhur., Khim.*, 1955, Abstr. No. 55,417) is adapted for the determination of Sn in mixed and fluorite ores. To 1 g of the finely ground ore add a few grains of zinc dust, treat with 1 drop of HCl (1:4), evaporate to remove excess of HCl, cool, add 4 or 5 crystals of dimethylglyoxime and again grind. In the presence of Sn a pinkish-red colour appears. The sensitivity of the detection is $\simeq 0{\cdot}5$ μg of Sn for mixed ores, and $\simeq 0{\cdot}1$ μg for fluorite ores. It is established that the resulting tin dimethylglyoximate sublimes readily on heating. This property is used for the detection of Sn in ores containing a large number of other elements. C. D. KOPKIN

2082. **Spectrophotometric determination of tin with phenylfluorone.** Masayoshi Ishibashi, Tsunenobu Shigematsu, Yuroku Yamamoto and Yasushi Inoue (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (8), 473–477.—The photometric determination of Sn^{IV} with phenylfluorone (**I**) (*cf.* Luke, *Anal. Abstr.*, 1957, **4**, 67) was examined. The reproducibility of the colour is improved by the addition of 10% tartaric acid soln. (1 ml per 50 ml). The colour fades at room temp., the rate increasing with rise of temp. Interference is caused by Ti^{4+}, Sb^{3+}, Mo, Ge and a large amount of Al, whilst Zn, Mn, Ni and As^{5+} affect the colorimetry only slightly. The working curve is linear for $< 2{\cdot}0$ μg of Sn per ml. K. SAITO

2083. **Polarographic determination of tin in ores in the presence of lead.** D. Weiss (Res. Inst. of Ores, Prague). *Chem. Listy*, 1958, **52** (9), 1817–1819.—*Procedure*—Mix the sample (0·5 to 2·5 g) intimately with a sevenfold excess of a fusion mixture ($KNaCO_3$ + S) (2:1) in a covered porcelain crucible; heat gently for 20 min. and then strongly for 15 min. Boil the crucible and its contents in 100 to 150 ml of H_2O. To the liquid add 30 pellets of NaOH and heat for 15 min. at 80°. Dilute to 250 ml with H_2O and filter through a paper filter. Take an aliquot, add 30 pellets of NaOH and oxidise dropwise with H_2O_2 (30%) till the soln. decolorises. Add H_2O_2 in excess (5 ml) and set aside for 15 min. Repeat the oxidation if necessary. Remove H_2O_2 by boiling, cool, add conc. HCl (30 ml) and add

$KMnO_4$ soln. (5%) dropwise until pink. Add conc. HCl (20 ml) and powdered iron (0·5 g) and set aside for 10 min. Add hot 6 *N* HCl (100 ml) and boil until the iron is dissolved. Add a saturated soln. of $HgCl_2$ (0·5 ml) and NaH_2PO_2 soln. (50%) (15 ml) and boil till the ppt. settles. Add a small amount of $NaHCO_3$, dilute with hot 6 *N* HCl, cool, add a further portion of $NaHCO_3$, then gelatin soln. (0·5%) (3 ml) and adjust the vol. to 250 ml with 6 *N* HCl. Transfer 10 ml of the supernatant liquid into a polarographic cell, remove O with N and register the wave from − 0·2 to − 0·6 V. Evaluate the result by the method of standard addition. In the presence of large amounts of SiO_2 the use of fuchsine soln. (1%) (5 ml) instead of gelatin is preferred. The method is suitable for the determination of 0·01 to 10% of Sn in ores. J. ZÝKA

2084. **Detection of tin and antimony in semi-micro analysis.** H. Menzel and G. Siewert. *Mikrochim. Acta*, 1958, (6), 814–815.—The original reaction of Fresenius (*Z. anal. Chem.*, 1862, **1**, 444) for the detection of Sn and Sb with metallic zinc on platinum foil may be modified by the application of 'inner electrolysis' using metals less noble than platinum as separating electrodes provided that such metals are at least as noble as Sb. Copper foil is a possible electrode material, whilst aluminium wire is now available and convenient for use as the solution electrode. Procedures for carrying out the modified tests are described. D. F. PHILLIPS

2085. **Determination of oxide films on tin-plate.** A. R. Willey and D. F. Kelsey (American Can Co., Barrington, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1804–1806.—The coulometric-reduction cell and procedure described is a modification of earlier methods (*cf. Anal. Abstr.*, 1958, **5**, 2570). Oxygen is rigidly excluded and very dil. HBr soln. replaces neutral KCl soln. as electrolyte; a recording potentiometer obviates the manual plot of data. With a sample of 4 sq. in., a constant current of 1 mA at 254 V is used. The reference electrode is a silver wire, forming a silver - silver chloride half-cell in the electrolyte. The accuracy was verified (for 4 to 40 milli-coulomb equivalents of SnO_2) by the oxalic acid dissolution - polarographic analysis method. W. J. BAKER

2086. **Gravimetric determination of lead.** D. Pirtea and G. Baiulescu. *Comun. Acad. Rep. Populare Romîne*, 1957, **7**, 329–333.—A 20% soln. of Na 4-aminosalicylate was used as a reagent for the pptn. of Pb, yielding fine white crystals of $Pb(C_7H_6O_3N)_2$. The ppt. was washed first with a 4% soln. of the reagent, then with ethanol and ether, and dried and weighed. A factor of 0·40513 was used for the calculation. The presence of Na^+ does not influence the accuracy of the determination, but NH_4^+ must be eliminated before pptn. CHEM. ABSTR.

2087. **Polarographic determination of lead in ores.** D. Weiss (Res. Inst. of Ores, Prague). *Chem. Listy*, 1958, **52** (9), 1814–1815.—*Procedure*—Boil the sample (0·5 to 1 g) for 5 min. with conc. HCl (30 ml) till all H_2S is removed. Cool, add $KClO_3$ (0·5 g), set aside (3 min.), then boil for 3 min. In the presence of Sn a further addition of HCl and $KClO_3$ must be made and the soln. evaporated to dryness. Add conc. HCl (10 ml) and heat on a sand bath at 80° till the vol. is reduced to 10 ml. Cool, add dil. HCl (3:2) (40 to 50 ml) and heat for 15 min. on a sand bath at 90°. Wash into a flask by means of a small vol. of H_2O, add 15 ml of HCl (3:2), dilute to 100 ml with the same acid, add saturated $HgCl_2$ soln. (0·5 to 1 ml), NaH_2PO_2 soln. (50%) (5 to 10 ml) and heat till all dissolves. Add a small amount of $NaHCO_3$ and gelatin soln. (1%) (5 to 10 ml), dilute to a suitable vol. with H_2O, mix, and set aside for 1 to 2 hr. Measure 5 to 10 ml of the supernatant liquid into the polarographic vessel, remove O with N, and register the wave from −0·3 to −0·7 V. Compare the wave with a blank to which a known amount of $Pb(NO_3)_2$ soln. has been added. The method described is rapid and simple and suitable for samples containing 0·2 to 20% of Pb, but yields results about 0·02 to 0·05% lower than those of gravimetric determinations. Large amounts of Cu and Sb in the sample can be removed by means of powdered iron. J. ZÝKA

2088. **Photometric determination of titanium.** M. Ziegler, O. Glemser and A. von Baeckmann (Anorg.-Chem. Inst. der Univ., Göttingen). *Angew. Chem.*, 1958, **70** (16), 500–502.—Small amounts of Ti can be determined with tributylammonium acetate (**I**) and sulphosalicylic acid (**II**) in the presence of many other ions; Fe^{III} must be reduced to Fe^{II} and Mo removed. *Procedure*—To 25 ml of weakly acid soln. containing up to 0·5 g of ferric salt and 2 mg of molybdate add 2·5 ml of 10% aq. **II** soln., 2 ml of 20% $Na_2S_2O_3$ soln. and 10 ml of 20% $NaHSO_3$ soln. Boil, cool to 40° or 50°, add 2 ml of $Na_2S_2O_3$ soln. and cool. To remove Mo, shake the soln. with 5 ml of 4% aq. thioglycollic acid and extract first with dichloromethane, then with $CHCl_3$. To determine Ti in the aq. phase, add 5 ml of **II** soln., adjust the pH to between 3·5 and 4 with Na acetate - acetic acid buffer, and add 10 ml of **I** soln. Extract with 8 ml of $CHCl_3$, add 5 ml more of **I** soln. and extract again with 6 ml of $CHCl_3$. Wash the aq. phase with 4 to 5 ml of $CHCl_3$, make the total extract up to 20 ml and measure at 400 mμ. Results given for steel, alloys, rocks and glass agree well with those obtained by other methods. P. D. PARR-RICHARD

2089. **Polarographic determination of titanium in alluvial sands.** L. Stănescu. *Rev. Chim., Bucharest*, 1958, **9** (7–8), 460–461.—The principle of the method is the reduction of Ti^{IV} in complexes formed with oxalic acid to Ti^{III} by the dropping-mercury cathode. To separate the Ti from the many other metals, in particular Fe, the soln. is first electrolysed with a mercury cathode, followed by oxidation with HNO_3 of any reduced Ti. The influence of the concn. of H_2SO_4 and gelatin on the diffusion current, the displacement of $E_{\frac{1}{2}}$ by oxalic acid, and the effect of pH were studied. For the polarographic determination, oxalic acid (0·2 *M*) with H_2SO_4 (0·5 *M*) is recommended as electrolyte. *Procedure*—The sample (1 g) containing 1 to 60% of Ti is separated from SiO_2 by a mixture of H_2SO_4 and HF. The residue is fused with 10 g of potassium pyrophosphate, the melt is dissolved in H_2SO_4 (1:3) and diluted to 250 ml. A 50-ml aliquot is electrolysed with a mercury cathode, at 4 to 6 V and 8 to 10 amp., the electrolysis being stopped 10 min. after a spot-test with NH_4SCN shows only traces of Fe. The soln. is then heated until fuming with 2 to 3 ml of conc. HNO_3, then diluted to 50 ml and warmed to dissolve sulphates, and made up to 100 ml. An aliquot is neutralised with aq. NH_3 to methyl orange, then treated with 2·8 ml of conc. H_2SO_4 (*d* 1·84). To the cooled soln. are added 20 ml of oxalic acid (*M*) and 1 ml of gelatin soln.

(0·5%), and the mixture is made up to 100 ml and analysed polarographically at 0 to 0·8 V, the pH being controlled at 0·5. Oxygen is removed by bubbling methane through the soln. The optimum concn. of Ti is 0·3 to 18 mg per 100 ml. For concn. $> 1\%$, the max. error is $\pm 4\%$, but for concn. $< 1\%$ the errors are too high for the method to be of value. H. SHER

2090. **Rapid photometric determination of titanium in copper alloys.** H. Wiedmann. *Z. Metallk.*, 1957, **48**, 410–412.—Dissolve 0·5 g of filings in HCl - HNO_3 (1:1) (10 ml). After diluting the soln. to 100 ml, 5 ml is mixed with 10 ml of ascorbic acid, 30 ml of water, 2 ml of chromotropic acid, and 10 ml of buffer soln. The pH value is subsequently adjusted with HCl (1:4) or NaOH soln. (20%) to 2·5. The soln. is then diluted to 100 ml with water and the extinction measured through a S47E filter. The calibration with standard soln. is described. CHEM. ABSTR.

2091. **Volumetric - gravimetric determination of titanium in steel.** V. V. Evdokimov. *Uch. Zap. Kazansk. Univ.*, 1957, **117** (9), 204–206; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,249.—A procedure is described for the determination of Ti in steel by titration of $TiCl_3$ with 0·01 *M* methylene blue (Porfir'ev *et al.*, *Zhur. Anal. Khim.*, 1949, **4**, 114). Dissolve about 1·1 to 1·4 g of sample by warming with 2 *N* H_2SO_4, pass H_2S to remove Cu and Mo, filter, add to the filtrate 2 to 5 drops of H_2O_2 or cryst. $(NH_4)_2S_2O_8$ and pour it into 50 ml of KOH soln. warmed to 70° or 80°. Filter off the ppt. of the hydroxides of Ti and Fe, wash it with hot water and dissolve it in 10 to 15 ml of conc. HCl. Make the resulting soln. up to 50 ml and titrate a 5- or 10-ml aliquot (after reduction with zinc in an atmosphere of CO_2) with 0·01 *M* methylene blue. The analysis takes 50 to 70 min. C. D. KOPKIN

2092. **Photometric determination of titanium dioxide in inclusions.** L. Brháček and A. Golonka (Research Inst. VŽKG, Ostrava, Czechoslovakia). *Hutn. Listy*, 1958, **13** (9), 811–812.—The reaction with chromotropic acid has been used for the photometric determination of Ti in inclusions. *Procedure*—Decompose the sample, remove SiO_2, melt the residue with $K_2S_2O_7$, dissolve the residue in H_2O with addition of a small amount of H_2SO_4 and dilute to 100 ml. To a 10-ml aliquot add 10 ml of ascorbic acid soln. (20 g of ascorbic acid and 20 g of $Na_2SO_3.7H_2O$ diluted to 1 litre with H_2O) and 2 ml of the reagent (dissolve 3 g of chromotropic acid in 100 ml of H_2O and add 1 g of Na_2SO_3), heat to 60°, cool, add 10 ml of buffer soln. (Na acetate - acetic acid) and adjust the pH to 2·8 to 3·3. Transfer to a 100-ml flask and dilute to vol. with H_2O. Measure the extinction with the use of a blue filter. Compare with a calibration curve. J. ZÝKA

2093. **Vacuum extraction method for the determination of the hydrogen content of titanium.** V. I. Lakomskiĭ. *Avtomat. Svarka*, 1958, (2), 81–91; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,290.—A method is described for the determination of H in titanium, based on the vacuum extraction of the sample at 800°. Clean the sample of metallic titanium (0·3 to 0·5 g) on an emery wheel, wash it successively with CCl_4, ethanol and ether, place it in a container of iron or molybdenum sheet and insert it in the reaction tube, which has been previously de-gassed for 30 to 45 min. at 900°. Evacuate the tube to 10^{-2} torr and de-gas under vacuum for 3 min. Heat the tube with a nichrome resistance heater and periodically (usually every 5 min.) take several measurements of the pressure of the evolved gas. The described method does not require complicated apparatus and is simple to carry out. It is established experimentally that the optimum temp. of heating is 800°. The results of the determination of H agree satisfactorily with those of the vacuum-fusion method. The proposed apparatus may also be used for determining H in steel and cast iron. C. D. KOPKIN

2094. **Micro-detection by the use of ion-exchanger granules. Detection of zirconium with catechol violet.** Toshiko Ichikawa, Hayanari Shimoda, Takeo Murase and Hidetake Kakihana (Natsuka Secondary School, Nishi-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 989–996.—Catechol violet (**I**) is firmly adsorbed by a strong anion-exchange resin of a low cross-linkage (*e.g.*, Amberlite IRA-411, SO_4^{2-} form, 30 to 50 mesh) and can be used for the detection of Zr. In the presence of $> 0{\cdot}01$ μg of Zr, the yellowish-orange colour of the resin deepens; the change is most sensitive in *N* H_2SO_4. **I** is also adsorbed by a cation-exchange resin (*e.g.*, Amberlite IR-112, Na form) and its sensitivity for the detection of Zr is greater than by the use of **I** in soln. Interference results from Bi, Hg, Fe^{3+}, Al and Cu. *Procedure*—A few granules of Amberlite IRA-411 (SO_4^{2-}) are mixed on a porcelain tile with one drop each of *N* H_2SO_4 - *M* K_2SO_4 (3:1), aq. **I** soln. (0·5%) and an acid (0·1 *N*) soln. of the sample. K. SAITO

2095. **The extraction of zirconium with tri-*n*-octylphosphine oxide and its direct determination in the organic phase with catechol violet.** J. P. Young and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1958, **1** (3), 263–275.—The Zr - catechol violet (**I**) complex in tri-*n*-octylphosphine oxide (**II**) - *cyclo*hexane - abs. ethanol absorbs at 655 mμ; Beer's law is obeyed for $> 1{\cdot}0$ μg of Zr per ml. When Zr is extracted from a chloride medium, Al, U, V, Fe, Cr, Pb, Ni and Co, among other metals, do not interfere, especially if NH_4SCN is added. Some Th may be present, and milligram amounts of SO_4^{2-} and PO_4^{3-}; Mo, Ti and Hf interfere. By extracting from a nitrate medium, Al, Ti, Mo, V, Fe, Cr, etc., do not interfere, but U, Th and Hf do. Only microgram amounts of SO_4^{2-} and PO_4^{3-} may be present. The choice of extraction medium should be based on the presence or absence of Th, U, Mo, Ti, SO_4^{2-} and PO_4^{3-} in the aq. sample. *Procedure*—(*i*) Make the soln. $\simeq 7$ *M* to HCl giving a final vol. of > 25 ml containing > 125 μg of Zr. Add 700 mg of NH_4SCN and extract for 10 min. with 5 ml of 0·01 *M* **II** in *cyclo*hexane; some HCN may be produced by decomposition of NH_4SCN. Transfer 1 to 3 ml of the organic phase to a 25-ml flask, add 10 ml of abs. ethanol, 1 ml of 0·05% **I** and 5 ml of pyridine. Dilute to the mark with ethanol and read at 655 mμ against ethanol. (*ii*) Make a similar aliquot $\simeq 7$ *M* to HNO_3 and extract for 10 min. with 5 ml of 0·02 *M* **II** in *cyclo*hexane. Transfer 1 to 2 ml of the organic phase to a 25-ml flask and continue as for the extraction from HCl. P. D. PARR-RICHARD

2096. **Determination of zirconium in alluvial sands.** R. Petcov and G. Răducan. *Rev. Chim., Bucharest*, 1958, **9** (7–8), 459.—A gravimetric method in which Zr mandelate is used, and a colorimetric

method in which alizarin red S is used, are described. Separation of other elements is not necessary. The sample of finely ground sand (1 to 2 g) is treated with 30 ml of a mixture of H_2SO_4 and HF (1:10), evaporated to dryness and re-dissolved 4 times, and the residue finally heated with 10 g of molten $Na_2B_4O_7$. The cooled melt is dissolved in 150 ml of HCl (1:5), then boiled, cooled and diluted to 250 ml. *Gravimetric procedure*—A 100-ml portion of the resulting soln. with 10 ml of HCl (conc.) and 50 ml of a mandelic acid soln. (16%) is warmed for 30 min. on a water bath at 85° with occasional stirring, then allowed to cool, and the white ppt. is filtered off. The ppt. is washed with a soln. of HCl (2%) and mandelic acid (5%), then two to three times with small quantities of ethanol, and the crucible and ppt. are dried at 110° to 120°. *Colorimetric procedure*—Two 10-ml aliquots of the soln. obtained as described above are each treated with 2 ml of a soln. of hydroxylamine hydrochloride (25%), warmed for 2 to 3 min. on a water bath until decolorised, then cooled, and 2·5 ml of HCl (10%) is added. To one soln. is added 1 ml of 0·05 *M* EDTA with stirring and, to both soln., 5 ml of alizarin red S (0·1%). Both soln. are then warmed in the water bath for 3 min., cooled, diluted to 50 ml, and their extinctions are measured against EDTA soln., a 5-ml cell and 570-mμ filter being used. Results are referred to a calibration curve.

H. Sher

2097. **Complexometric determination of lead in bearing metals and solders.** K. Študlar and I. Janoušek (Res. and Control Inst. ZVIL, Plzeň, Czechoslovakia). *Hutn. Listy*, 1958, **13** (9), 805–808.—A direct complexometric determination of lead in alloys with the use of Eriochrome black T or methyl thymol blue as indicator has been worked out. The described method is suitable for all kinds of lead-base alloys containing > 10% of Pb and requires only 45 min. *Procedure*—Dissolve the sample (0·5 g) in conc. HCl (20 ml) by heating. Cool and add in portions H_2O_2 (30%) (5 ml) till clear and yellow - green. Remove H_2O_2 by heating, evaporate to 5 ml and cool. Add tartaric acid soln. (20%) (20 ml), dilute with H_2O (100 ml), neutralise with aq. NH_3 to methyl red, mix till the $PbCl_2$ dissolves, add KCN (for masking Cu, Ni, Cd and Zn), 5 ml of 0·025 *M* soln. of the Mg salt of EDTA, and Eriochrome black T or methyl thymol blue as indicator and titrate with 0·05 *M* EDTA (disodium salt) till blue. The mean error is ± 0·15% for 20 to 90% of Pb. Bismuth (> 10 mg in the soln.) causes interference.

J. Zýka

2098. **Preliminary experiments on the radiometric estimation of traces of thorium.** K. R. Kar and B. C. Sawhney (Univ., Delhi). *J. Sci. Ind. Res., B, India*, 1958, **17** (9), 365–366.—The estimation of traces of Th (up to 30 μg) is achieved by measuring the radioactivity of labelled P in chemical combination, as pyrophosphate, with Th; AgI (produced *in situ*) in dil. HNO_3 (0·3 *N*) and containing excess of I^- is used as a carrier for ThP_2O_7 (^{32}P). The estimation can be completed within an hour with an accuracy of ± 2%.

I. Jones

2099. **Determination of thoron (thorium emanation) in soil air.** V. V. Cherdyntsev. *Trudy Radiev. Inst., Akad. Nauk SSSR*, 1957, **6**, 34–40; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,746.—With a sufficiently high content of ^{228}Th in the soil air, it is possible to determine ^{228}Th directly when the ionisation effect of ^{228}Th is greater than that of Rn. Draw a continuous stream of the air at a const. rate (v) (3 to 4 litres per min.) through a probe inserted to a standard depth of 1 to 3 metres in the soil, and then through a drying system and the ionisation chamber of the measuring apparatus. After a few minutes a dynamic radioactive equilibrium between ^{228}Th, Rn and their disintegration products is set up in the air stream. The amount of disintegrated Rn reaches a maximum value at very low v (≃ 1 ml per min.); the influence of actinon is negligible, because of its small content. After measuring the total ionisation effect (Q') in the air, cut off the flow, close the ionisation chamber and, after a certain time (≃ 10 min.), sufficient for the practically complete disintegration of ^{220}Th, measure the ionisation effect (Q_{Rn}) caused by the Rn remaining in the ionisation chamber. Then $Q_{^{228}Th} = Q' - Q_{Rn}$. Calibrate the apparatus by drawing air at a standard rate through a standard sample of Th and finding the conversion factor between the ionisation current I_0 and the number of atoms of ^{228}Th decomposed, and therefore the number of atoms of ^{228}Th (N_0) which cause a value of I_0 corresponding to one division per minute on the instrument scale. Having measured the activity of the soil air causing an ionisation current I_1, calculate the concn. of atoms of ^{228}Th per litre of soil air from the equation $Q = \lambda N_0 I_1 / v I_0$. The normal content of ^{228}Th per litre of soil air corresponds to equilibrium with a few mg of Th. To measure small amounts of ^{228}Th in soil air in the presence of large amounts of Rn, draw the stream of air through the same measuring apparatus for a considerably longer period (from 1 to 7 or 8 hr.). Periodically check the value of the ionisation current, the variations in which, after correcting for the growth of an active ppt., indicate the variations in the activity of the soil air. After cutting off the flow, measure the ionisation current in the closed ionisation chamber in the same way as for the emanation method. Then evacuate the emanations from the chamber and obtain the disintegration curve of the active ppt. which has settled on the charged plate of the ionisation chamber. This curve asymptotically approaches the disintegration curve of the B products, which are in equilibrium with their disintegration products. After a certain time T (≃ 30 min.) measure the ratio of the ionisation currents from ThB and RaB—$I_{ThB}/I_{RaB} = \xi_T$. Having determined ξ_{30}, calculate the ratio of the number of atoms of Th to the number of atoms of U from the empirical expression $N_{Th}/N_U = 100\,\xi_{30}$. The normal value of ξ_{30} for soil air is ≃ 0·1. The sensitivity of this method is a few tens per cent lower than that of the direct method, but it is the only reliable field method for determining small amounts of ^{228}Th in soil air in the presence of Rn.

C. D. Kopkin

2100. **Extraction of nitrates by tri-*n*-butyl phosphate. III. Extraction at trace concentrations.** E. Hesford and H. A. C. McKay (A.E.R.E., Harwell, Berks., England). *Trans. Faraday Soc.*, 1958, **54** (4), 573–586.—A theory of the extraction is developed based on the observation that nitrates of metals (lanthanides, actinides, zirconium) mainly exist in the tri-*n*-butyl phosphate (**I**) phase as a single molecular form $M(NO_3)_p.qI$ [*e.g.*, $M(NO_3)_3.3I$, $M(NO_3)_4.2I$ or $MO_2(NO_3)_2.2I$] with a fixed number of solvent molecules and no water of hydration. *Procedure*—(*i*) The concn. of **I** was varied by adding an inert diluent. The results obtained were used to determine the solvation number q. (*ii*) The HNO_3 concn. was varied. In certain cases the partition coeff. measured was used to calculate

the thermodynamic equilibrium const. and the activity coeff. of a trace of the extractable nitrate in a HNO_3 medium. Reasonable functions were obtained for the activity coeff. (*iii*) An unextractable nitrate, $NaNO_3$, was added as a salting-out agent. The theory of nitrate extraction by **I** made it possible to estimate the resulting rise in partition coeff. Partition coeff. ratios for pairs of similar elements were determined. K. R. C.

2101. **Use of nitrosophenol complexes in the detection and determination of nitrites.** S. M. Peach (Rugby Coll. of Technol. and Arts, Eastlands, Rugby, England). *Analyst*, 1958, **83**, 644–647.—Resorcinol (5 g) and $(NH_4)_2SO_4.FeSO_4$ (5 g) are dissolved in separate 5-ml portions of glacial acetic acid and each soln. is diluted to 100 ml. One drop each of nitrite soln., resorcinol soln. and ferrous soln. are mixed, in that order, on a white tile. A green colour develops in 10 min. and is just discernible with 0·5 μg of NO_2^-. In a quant. experiment, 20 ml of a soln. containing 0·1 g of NO_2^- was diluted to 95 ml, 0·2 g of resorcinol was dissolved in the soln. and 1 ml of glacial acetic acid was added, followed immediately by 0·2 g of $(NH_4)_2SO_4.FeSO_4$. The liquid was diluted to 100 ml and after 10 min. its extinction graph was plotted. Calibration graphs were prepared at 690 mμ. In a similar method in which $CoSO_4$ is used instead of the Fe salt, the extinction graph of the *iso*amyl alcohol extract of the complex had an absorption max. at 396·2 mμ. Copper, Ni and Fe can be tolerated only up to stated amounts, but a limited excess can be removed by pptn. with Na_2CO_3. A soln. of *m*-methoxyphenol can be used in place of resorcinol and the green complex with Fe^{3+} can be extracted with *iso*amyl alcohol (705 mμ to 710 mμ). The method is somewhat less sensitive than the Griess method, but is easier of application. A. O. Jones

2102. **Arsenometric determination of nitrite and ammonium ions.** A. Kellner, S. Szabo and L. Szekeres (Univ. Agric. Sci., Budapest). *Magyar Kém. Foly.*, 1958, **64** (9), 355–356.—Nitrite is oxidised with bromide - bromate; NH_4^+ are oxidised with NaOBr. The excess of oxidising agent is titrated in acid soln. with As_2O_3 soln., with IO_3^- or IBr and starch as indicator. A. G. Peto

2103. **Rapid routine analysis of iron pickling liquor. V. Rapid determination of sodium nitrate and nitrite, chromium and iron in fused caustic salts.** Kimio Mukaewaki (Nippon Tokushu Steel Tube Co., Funato, Itabashiku, Tokyo). *Japan Analyst*, 1958, **7** (8), 491–496.—Samples (5 to 10 g) of fused caustic salts, used for the de-scaling of stainless steel, are cooled, weighed and dissolved in hot water (100 ml) and the soln. is filtered into a measuring flask (250 ml). Nitrate and nitrite are reduced with Fe^{2+} in dil. H_2SO_4 and the excess of Fe^{2+} is titrated with $KMnO_4$. Chromium is oxidised to CrO_3 with $HClO_4$ and determined volumetrically by the usual method. Iron is determined in the residue by the usual method. The time taken for a determination is $<$ 50 min. K. Saito

2104. **Paper chromatography of phosphorus compounds. I. Inorganic phosphorus compounds.** H. Hettler (Univ., Heidelberg, Germany). *J. Chromatography*, 1958, **1** (5), 389–410 (in German).—A review of the requisite conditions for the paper chromatography of inorganic phosphorus compounds and of procedures for the identification and determination of condensed phosphates and lower phosphorus oxy-compounds is presented. The choice of solvent systems, the treatment of the paper and other special conditions are discussed. G. Burger

2105. **Colorimetric detection of arsenic as copper arsenide.** J. T. Stock and L. M. Garcia (Univ. of Connecticut, Storrs). *J. Chem. Educ.*, 1958, **35** (8), 401.—The procedure on a vol. of 0·5 ml and the apparatus used are described. By addition of 4 *N* H_2SO_4 to the sample in ths presence of zinc, AsH_3 is liberated. On paper treated with 10% $CuSO_4$ soln., the Cu_3As_2 appears as a dark stain within 2 min., and with quantities $>$ 2 mg within 40 sec. Antimony and tin do not interfere. O. M. Whitton

2106. **Data on reaction kinetics. Autoxidation of iodine in solutions of mercury(II) salts. Potentiometric titration of arsenic and antimony with a standard solution of iodate.** J. Bognár and S. Sárosi (Tech. Univ. for Heavy Indust., Miskolc, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (1), 1–13 (in English).—A theoretical discussion of the autoxidation of iodine in soln. of Ag and Hg^{II} salts is given, and applied to the determination of As and Sb. In soln. acidified with HCl or H_2SO_4, the oxidation of As^{3+} by IO_3^- follows the equation

$$5As^{3+} + 2IO_3^- + 12H^+ = I_2 + 5As^{5+} + 6H_2O,$$

and similarly for Sb. If, on reaching this end-point, the acidity is raised with conc. HCl to 4 to 6 *N*, a second end-point can be reached, according to the equation—

$$2I_2 + IO_3^- + 6H^+ + 5Cl^- = 5ICl + 3H_2O.$$

Both end-points can be detected potentiometrically, with a platinum indicator electrode and a reference electrode of HgCl or $HgSO_4$, according to the acid originally used for acidification. In the presence of a Hg^{II} salt (*e.g.*, 10 to 25 ml of saturated $HgSO_4$ in *N* HCl), the reaction follows the equation—

$$3As^{3+} + IO_3^- + 6H^+ = I^- + 3As^{5+} + 3H_2O,$$

and similarly for Sb. The acidity should be 0·5 to 2·0 *N* in HCl for As, and $<$ 3·5 *N* for Sb (in the presence of tartrate if the concn. of HCl is low). If, after reaching this end-point, the HCl concn. is raised to 4 to 6 *N*, I^- are released from the HgI, and the titration can be carried to the ICl end-point as before. When AgCl replaces $HgSO_4$, Sb can be titrated to the iodide stage, in 0·5 to 1·5 *N* HCl, with a gold plate as indicator electrode, and As similarly in 0·5 to 2·0 *N* HCl, with a platinum wire as indicator electrode, the reference electrode being $K_2SO_4|Hg_2SO_4|Hg$. The titrations can be carried to the ICl stage in 4·5 to 5·5 *N* HCl but, since the end-point is slow, and negative errors up to 1·2% are found, the mercury method is preferred. R. E. Essery

2107. **Polarographic determination of antimony.** D. Weiss (Res. Inst. of Ores, Prague). *Chem. Listy*, 1958, **52** (9), 1815–1817.—*Procedure*—To the sample (0·5 to 2 g) add conc. HNO_3 (15 to 20 ml) and after 5 min. dissolve with heating on a sand bath. Cool, add conc. H_2SO_4 (10 ml), evaporate to fumes, add H_2O (10 to 15 ml) and evaporate to a syrup. Cool, add H_2O (10 ml), heat and neutralise with 10 *N* NaOH till a turbidity appears. Add 20 pellets of NaOH, saturated Na_2S soln. (20 to 25 ml), mix, boil for 3 min., dilute with H_2O (70 ml) and heat at 100°. Dilute to 250 ml with H_2O. Filter, and to 50 ml of the filtrate add 10 pellets of NaOH, dissolve and oxidise while cooling with H_2O_2

(30%) until colourless. Add H_2O_2 in excess (2 ml), set aside for 10 min. and destroy H_2O_2 by boiling. Add conc. HCl (15 ml), cool and add $KMnO_4$ soln. (5%) until pink. Add one drop of $KMnO_4$ soln. in excess, then conc. HCl (50 ml) and heat for 3 to 5 min. to remove the excess of Cl. Add HCl (3:2) (100 ml), saturated $FeCl_3$ soln. (one drop) and NaH_2PO_2 soln. (50%) (10 ml) and heat until colourless. If the soln. becomes grey or brown due to As add saturated $HgCl_2$ soln. (0·5 ml), heat and let the ppt. settle. Then dilute with HCl (3:2) free from oxidising compounds, cover and set aside for 15 to 20 min. Cool, add gelatin soln. (1%) (5 to 10 ml), dilute to 250 ml with HCl (3:2), mix and set aside for 1 to 2 hr. Transfer 10 ml of the supernatant liquid to the polarographic vessel, remove O with N and register the wave from 0 V to − 0·25 V. Evaluate the results by the method of standard addition. The method is suitable for the analysis of ores containing 0·1 to 10% of Sb in the presence of a large excess of Cu. J. ZÝKA

2108. **Micro-detection by the use of ion-exchanger granules. Detection of bismuth with catechol violet.** Takeo Murase (Ind. Res. Inst., Aichi Prefecture, Chokusa-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 983–989.—Catechol violet (**I**) is adsorbed either by a cation-exchange resin (*e.g.*, Dowex 50W) or by an anion-exchange resin (*e.g.*, Dowex 1-X1) and becomes more sensitive to Bi (limit of detection, $\simeq$ 0·05 μg) at pH 2 to 4. The orange colour of the anion-exchanger changes to dark or olive green according to the amount of Bi, whereas the orange of the cation-exchanger changes to red and then to violet. In the latter case, increase in ionic strength (*e.g.*, addition of KNO_3) decreases the sensitivity (0·04 μg). K. SAITO

2109. **Titrimetric determination of small amounts of bismuth as the reineckate.** I. L. Bagbanlÿ and I. G. Guseĭnov. *Izv. Akad. Nauk AzerbSSR, Ser. Fiz.-Tekh. i Khim. Nauk*, 1958, (1), 83–95; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,315.—In acid medium Reinecke's salt (**I**) precipitates Bi quant. as the complex $Bi[Cr(SCN)_4(NH_3)_2]_3$ (**II**). To determine Bi, dissolve this ppt. in 2 *N* HCl or hot 10% NaOH soln. and titrate the liberated SCN^- with KIO_3 or $AgNO_3$ soln. (or determine Cr). Acidify the soln. containing Bi with sufficient HNO_3 so that, after adding the precipitant, the acidity will be 0·04 to 1·29 *N*, add a freshly prepared 2·5% soln. of **I** (1 ml for each mg of Bi), set it aside in an ice bath for 15 to 20 min. and filter through a No. 4 Gooch crucible, transferring the crystals with a cold 1% soln. of **I**. Wash the ppt. 2 or 3 times with cold abs. ethanol or with a mixture of ethanol and benzene (1:1) and dissolve it on the filter in a hot 10% NaOH soln. Wash the filter with hot water, stand the filtrate for 5 or 10 min. on the boiling-water bath, add 10 ml of conc. HCl, cool under the tap, add 5 or 10 ml of benzene and titrate the SCN^- with KIO_3 soln. till the benzene layer is completely colourless. In the second variation, after dissolving the ppt. in 10% NaOH soln., acidify the resulting soln. with acetic acid and titrate with $AgNO_3$ soln. with eosin as adsorption indicator. In the third variation, after dissolving the ppt. of **II** in the NaOH soln., oxidise Cr^{3+} in the usual way and titrate iodimetrically. The iodimetric method is the most accurate and rapid. No interference is caused by the presence of the cations of the first to third analytical groups, PO_4^{3-} or AsO_4^{3-}. C. D. KOPKIN

2110. **Analytical use of 8-mercaptoquinoline (thio-oxine) and its derivatives. VI. The vanadium complex of thio-oxine and its properties. The colorimetric determination of vanadium.** Yu. A. Bankovskiĭ, E. M. Shvarts and A. F. Ievin'sh. *Izv. Akad. Nauk LatvSSR*, 1958, (3), 121–126; *Ref. Zhur., Khim.*, 1958, (24), Abstr. No. 81,316.—The analytical properties of thio-oxine (**I**) are studied. By the action of **I** in weakly acid soln. on vanadyl salts or ammonium metavanadate, V^V is reduced to V^{IV}, which reacts with excess of **I** to form vanadyl thio-oxinate (**II**), which separates as a light green ppt. of composition $VO(C_9H_6NS)_2$. **II** is easily soluble in most organic solvents, the extracts being yellow - green. The absorption curve of a soln. of **II** has three maxima, at 249, 272 and 412 mμ, with mol. coeff. of extinction of 30,800, 27,200 and 7400, respectively. Complete extraction of **II** takes place in the pH range 4 to 5·5. Beer's law is obeyed for up to 15 μg of V per ml. The formation of **II** may be used for the determination of small amounts of V in soln. and of its pure salts in the presence of U, W, Cr, Tl, As, Ni, Co, Cd, Hg, Ag, the alkali and alkaline-earth metals, and also in the presence of small amounts of Fe; Pb, Zn, Bi, Sb, Sn, Pt, Cu, Pd and Mn must first be removed. Of the usual anions, only oxalate ions in amounts > 0·5 mg in 50 ml interfere in the determination of V. To determine V with **I**, to 20 or 30 ml of neutral soln. add 10 ml of a saturated soln. of KHF_2 (to mask Fe), 10 ml of a 15% soln. of KCN (to eliminate the influence of Ni, Co, Cd, Hg and Ag), 30 ml of acetate buffer soln., 10% acetic acid to pH 5 and 5 ml of a 2% aq. soln. of the potassium salt of **I**, and extract **II** with 10 ml of toluene or xylene. Filter the extract through cotton wool and measure its extinction. Find the content of V from a calibration curve constructed in the presence of all the reagents. The experimental error is $\gtrsim \pm 4\%$. C. D. KOPKIN

2111. **Tests on microchemical determination of niobium and on niobium - tantalum separation by means of tetramethylenedithiocarbamate.** H. Malissa (Max Planck Inst. für Eisenforschung, Düsseldorf, Germany). *Mikrochim. Acta*, 1958, (6), 726–730.—Both Na diethyl- and Na tetramethylenedithiocarbamate react with Nb but not Ta in the pH range of 2 to 6. No perfect stoicheiometric gravimetric factor could be found for Nb, but satisfactory determinations can be made on the micro scale by the use of an empirical factor. Quantitative separation of Nb and Ta is possible. D. F. PHILLIPS

2112. **Semi-micro determination of tantalum with selenous acid.** F. S. Grimaldi and M. M. Schnepfe (U.S. Geol. Survey, Washington, D.C.). *Anal. Chem.*, 1958, **30** (12), 2046–2049.—Pptn. of Nb with H_2SeO_3 is avoided by the addition of tartaric and oxalic acids. Small amounts of Nb and Ti co-pptg. with Ta are determined colorimetrically. *Procedure for Ta*—Fuse 50 to 60 mg of ore in a quartz crucible with 1·5 g of $K_2S_2O_7$ and dissolve the melt in 30 ml of hot aq. tartaric acid soln. (5%). Filter and repeat the fusion on any residue. Combine the filtrates ($\gtrsim$ 85 ml total vol.) and make the total amount of tartaric acid present up to 3 g if necessary. Add 5 ml of H_2SO_4 (1:1), 22·5 ml of conc. HCl, 7·5 ml of 10% (w/v) oxalic acid dihydrate soln., 25 ml of 10% (w/v) H_2SeO_3 and H_2O to 150 ml. Cover the beaker and digest the contents at 100° for 2·5 to 3 hr. Add paper pulp, filter off and wash the ppt. with hot 10% (v/v) HCl, ignite

the ppt. in quartz at 900°, cool and weigh. Fuse again and re-precipitate once for contents of tantalum pentoxide < 15 mg, twice for contents between 15 and 30 mg; Nb and Ti in the filtrates are pptd. with cupferron. The method is applied to amounts of tantaloniobate ores containing up to 30 mg of tantalum pentoxide.

P. D. PARR-RICHARD

2113. **Analysis of peroxy compounds. V. Direct determination of peroxy compounds in the presence of each other with arsenous acid.** L. J. Csányi and F. Solymosi (Inst. for Inorg. and Anal. Chem., Univ., Szeged, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (1), 69–80 (in German).—Polarographic, amperometric, potentiometric and dead-stop methods, and the use of a platinum - carbon electrode pair, are discussed with reference to the determination of H_2O_2 (**I**), H_2SO_5 (**II**) and $H_2S_2O_8$ (**III**) in mixtures, with standard As_2O_3 soln. For successive determinations in a single sample, the liquid is acidified with H_2SO_4 to 1 to 2 *N*, treated with KBr (0·1 to 0·2 g) as a catalyst, and titrated with standard As_2O_3 soln. to determine **II**. To the soln. are then added 2 g of KBr, two drops of 0·01 *M* OsO_4 and 1 to 2 ml of 5% ammonium molybdate soln. as catalyst, and the content of **I** is determined. Finally, the H_2SO_4 concn. is increased to 20 to 25%, and **III** is determined at 60° to 70°. All three end-points are detected with polarised platinum electrodes, or with a platinum - carbon electrode pair. For the determination in two aliquots, **II** is determined in the first sample as described above. To the second sample, two drops of OsO_4 catalyst are added, **I** and **II** are determined together, then the acidity and temp. are raised and **III** is determined as described above. End-points are detected with a platinum - carbon pair. Results from known mixtures showed good recoveries of all three components. It is suggested that the procedure can be used to determine other peroxy compounds, and satisfactory results are quoted for the determination of mixtures of H_2O_2 and peroxyacetic acid, and of H_2O_2 and peroxyphosphoric acid.

R. E. ESSERY

2114. **Amperometric determination of microgram quantities of sulphide sulphur.** L. Levin and W. B. Swann (Res. and Development Lab., Socony Mobil Oil Company, Inc., Paulsboro, N.J., U.S.A.). *Talanta*, 1958, **1** (3), 276–280.—For microgram amounts of S^- the blank value for the iodine - starch end-point is too high. In the method described, the sulphide ppt. is allowed to react in a closed system with excess of iodine, and the end-point of the amperometric back-titration is found graphically. The procedure has been applied to the determination of S^- in de-oiled engine deposits. *Procedure for S^- in solids*—Heat a sample (< 10 μg of S^-) with 30 ml of HCl (1 : 1) and pass the gases into 30 ml of alkaline $Cd(OH)_2$ soln. (3·85 g of $CdCl_2.2H_2O$ and 0·3 g of NaOH in 1 litre of H_2O). Purge the flask with N until evolution of H_2S is complete. Add a known excess of KIO_3 soln. and 5 ml of conc. HCl, stopper quickly and mix. Cool the soln. and titrate it amperometrically, applying 110 mV across the twin platinum electrodes and titrating with 0·002 *N* $Na_2S_2O_3$ to a pale-yellow coloration, then plot the scale readings against total vol. *H_2S in air*—Pass a known vol. of air through a covered flask containing 2% Cd acetate soln. Add a known excess of KIO_3, then HCl, and proceed as before.

P. D. PARR-RICHARD

2115. **Quantitative oxidation of sulphur - oxygen anions.** R. A. Krause and D. H. Busch (McPherson Chem. Lab., State Univ., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1817–1819.—Thiosulphate, $S_2O_3^{2-}$, $S_4O_6^{2-}$ and $S_3O_6^{2-}$ can be quant. and rapidly oxidised to SO_4^{2-} with a 0·1 *N* soln. of Ce^{4+} in 2 *M* $HClO_4$ at 85° for ≯ 5 min. After cooling the soln. to 50°, the excess of Ce^{4+} can be back-titrated with a standard soln. of Na oxalate, the end-point being sharp (colourless to pink) with nitroferroin (0·025 *M*) as indicator. The $HClO_4$ should be added before the sample soln. so as to avoid pptn. of $Ce(SO_4)_2$. The accuracy is ≃ ± 1%; Cl^- and $S_3O_6^{2-}$ interfere by not being quant. oxidised.

W. J. BAKER

2116. **The simultaneous determination of some sulphur compounds. (Preliminary communication).** L. Szekeres (Univ. Agric. Sci., Budapest). *Magyar Kém. Foly.*, 1958, **64** (9), 357.—The simultaneous determination of H_2S (**I**), H_2S_x (**II**), $H_2S_2O_3$ (**III**) and H_2SO_3 (**IV**) is described. The first aliquot is oxidised with iodine; **III** needs 1 g-equiv. of iodine per mole; **I**, **II** and **IV** need 2 each. The second aliquot is oxidised by Br; **I** and **III** each need 8 g-equiv. of Br per mole and **IV** needs 2. For the oxidation of **II**, $8 + 6(x - 1)$ g-equiv. per mole of Br are needed. The third aliquot is acidified and boiled; then only the S from **II** and **III** remains, and this can be determined by oxidation with Br. The fourth aliquot is also oxidised with Br, the following number of moles of H_2SO_4 being formed for each mole of the S compounds present—**I**, 1; **II**, *x*; **III**, 2; **IV**, 1. The H_2SO_4 formed can be determined volumetrically by the method of Bakács (*Anal. Abstr.*, 1955, **2**, 3343) or of Szekeres and Bakács (*Anal. Abstr.*, 1956, **3**, 990). The concn. of the unknowns can be calculated from the equations obtained from the four titrations.

A. G. PETO

2117. **Determination of thiosulphate by the silver thiocyanate method.** N.-H. Schöön (Chalmers Tekniska Högskola, Göteborg, Sweden). *Acta Chem. Scand.*, 1958, **12** (9), 1730–1745 (in English).—Thiosulphate can be determined by shaking the soln. with an excess of solid AgSCN, and the SCN^- in soln. are determined colorimetrically as $Fe(SCN)_3$ (Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1953, **74**, 358). This method has been studied in relation to the determination of $S_2O_3^{2-}$ in spent liquor from sulphite cellulose cooking. The ionic species and their equilibrium concn. in the presence of H_2SO_3 and $NaClO_4$ have been studied. The time of shaking should be between 10 and 40 min. In the presence of H_2SO_3, addition of formaldehyde is necessary to obtain a stable colour. The determination cannot be made in the presence of alkali sulphites.

G. BURGER

2118. **Photometric determination of a micro amount of tellurium with sodium diethyldithiocarbamate and tributyl phosphate.** Mariko Inarida (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 968–971.—When Te^{IV} is extracted from a 3 to 6 *N* HCl soln. with tributyl phosphate (**I**) (*Anal. Abstr.*, 1959, **6**, 1710) in the presence of Na diethyldithiocarbamate (0·1% aq. soln.) (2 ml), the extinction of the organic layer at 340 mμ is proportional to concn. of Te of < 40 μg per 5 ml of **I**, and the extinction at 400 mμ to concn. of < 100 μg of Te. The colour begins to fade 5 min. after the extraction with **I**. Any Te^{VI} is readily reduced to Te^{IV} by boiling in HCl.

K. SAITO

2119. **Colorimetric determination of chromium with Carmoazine.** N. M. Kravtsova. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 161–168; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,260.—It is shown that Carmoazine (Acid Chrome red 2 C) (**I**) in H_2SO_4 medium reacts with $Cr_2O_7^{2-}$ with the formation of a red-violet colour, the intensity of which is proportional to the concn. of Cr. The optimum conditions for the visual determination of Cr are 0·008 to 0·010% of **I**; acidity 0·75 to 2 g-equiv. of H_2SO_4 per litre; heating for 10 min. at 100°. Standards are prepared from 0·1% **I** soln. (0·40 ml) and 5 *N* H_2SO_4 (1·00 ml) to which various amounts of a soln. of $K_2Cr_2O_7$ (10 μg per ml) are added and diluted to 5 ml. The detectable minimum is 0·3 μg of Cr per ml. In the photometric determination of Cr, the concn. of **I** in the analytical and standard soln. must be $\ll$ 0·012%, and the concn. of $H_2SO_4 \simeq 1$ g-equiv. per litre, and heating must be carried out for 15 min. at 70°, with subsequent cooling of the soln. The sensitivity of the reaction under these conditions is 0·2 μg of Cr per ml (mol. extinction coeff. at 619 mμ is 10,000). With a concn. of Cr of 1·4 μg per ml, the relative error is $\gtrsim \pm 2\%$. No interference is caused by the presence of V^V at concn. up to 12·5 μg in 25 ml; by Mn^{2+}, Co^{2+}, Ni^{2+} or Al^{3+} at concn. of 4000, 50, 60 and 320 μg per ml, respectively; nor by Mo^{VI}, NO_3^- or Cl^- at concn. up to 50, 8000 and 1000 μg per ml, respectively. Ferric iron interferes. The method has been tested on samples of steel containing 0·24 to 1·52% of Cr. In the photometric determination, the relative error is $\gtrsim$ 4·5% (average error 2·16%). C. D. KOPKIN

2120. **Use of EDTA (disodium salt) for the photometric determination of chromium in chromite.** Yu. I. Usatenko and E. A. Klimkovich. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958 **8** (11), 169–177; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,261.—The method is based on the photometry of aq. soln. of the complex of Cr with EDTA (disodium salt) (**I**) in an acetate buffer medium (pH $\simeq$ 4). The composition of the resulting complex in all cases corresponds to the ratio Cr:**I** = 1:1. To determine Cr, mix 0·2 g of the finely ground chromite in a porcelain crucible with 0·6 g of soda lime and 0·4 g of MgO (or mix 0·2 g of ore with 0·4 g of MgO and 0·4 g of Na_2CO_3). Place the mixture in a crucible containing a layer of CaO or MgO and ignite at 1100° for 10 to 15 min. Moisten the baked mass with water, dissolve it in 25 ml of HCl (1:1) [or 40 ml of H_2SO_4 (1:4)], heat to $\gtrsim$ 70° and make up to 100 ml. To a 10-ml aliquot add 0·2 to 0·3 g of solid Na_2SO_3, boil for 1 min., add 20 to 25 ml of 0·1 *M* **I**, heat almost to boiling-point, neutralise with conc. aq. NH_3, maintaining the temp. at 60° to 80°, till the red-violet colour changes to blue-violet, boil for 1 min., dilute to 100 ml with buffer soln. (20 ml of 2 *N* Na acetate and 80 ml of 2 *N* acetic acid), and measure the extinction with a green filter. No interference is caused by the presence of Ca, Mg, Al, SiO_2 and Cu (at concn. up to a few per cent.); the influence of Fe is removed by the use of the green filter. The method has been tested in the analysis of several samples of chromite. The results of the titrimetric and photometric determinations are in good agreement. C. D. KOPKIN

2121. **New method for the titration of the chromic anion.** M. Mitrănescu. *Acad. R.P.R., Baza Cercet. Ştiinţ. Timişoara, Stud. Cercet. Ştiinţ., Ser. I*, 1957, **4**, 79–83.—The $HCrO_4^-$ are reduced in a hot acidic soln. with a known excess of a titrated soln. of H_2SO_4-hydrazine. The excess of reagent is titrated iodimetrically in the presence of K Na tartrate. The method is very accurate for quantities from 0·007 to 0·035 g of $HCrO_4^-$ and in soln. 0·1 to 0·02 *N* and an acidity of 0·16 to 1·0 *N*. An advantage of this method is the great stability of all the reagents used. This method is particularly well adapted to the determination of Cr in steel. CHEM. ABSTR.

2122. **Spectrographic-luminescence determination of chromium in synthetic rubies.** P. P. Feofilov and L. A. Kuznetsov. *Inzh.-Fiz. Zhur.*, 1958, **1** (4), 46–52; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,716.—The study is made on a series of samples in the form of polished parallel-sided plates containing 0·055 to 2% of Cr. The plates are cut parallel to the optical axis. The degree of polarisation of a series of chromium lines in the red and near i.r. regions has been studied photographically and has proved to be independent of the concn. of Cr. It is shown that in the luminescence spectrum of the ruby, increase of concn. of Cr causes an increase in the intensity of the i.r. region of the spectrum. The apparatus for recording the spectrum photoelectrically is described. The incident light falls on to the sample through a u.v. filter and a soln. of $CuSO_4$. The luminescent radiation passes through a lens on to a photomultiplier with an oxygen-selenium cathode. Insert in the parallel beam a Schott filter Rg-2, and also insert between the lenses an Rg-10 filter and an interference filter with max. transmission at 700 mμ to separate the doublet 692·7 and 695·2 mμ. Measure the photo-current and obtain the ratio of the photo-currents on the introduction of the Rg-10 filter and the interference filter. Standards are necessary for carrying out the analysis. The error of the analysis is + 5%. The dependence of the intensity of the radiation on the temp. is studied; it is shown that with increase of temp. the intensity decreases. C. D. KOPKIN

2123. **Determination of molybdenum in uranium and in molybdenum-uranium and molybdenum-niobium mixtures.** C. O. Granger (Res. and Development Branch, U.K.A.E.A., Culcheth, nr. Warrington, Lancs., England). *Analyst*, 1958, **83**, 609–615.—The complex of Mo with toluene-3:4-dithiol is formed in an aq. solvent medium in which it is soluble and solvent extraction is thus avoided. Two procedures are described, one, the difference method, in which the extinction at 680 mμ of the soln. of the complex is compared directly with that of simultaneously prepared standard soln., and one in which it is measured against water or a reagent blank and referred to that of standard soln. The soln. of the sample in HCl is cleared with H_2O_2, evaporated just to dryness without boiling, the residue is dissolved in HCl and the filtered soln. is diluted so that a 10-ml aliquot contains 100 to 110 μg of Mo for the difference method or $\gtrsim$ 30 μg for the alternative method. To this aliquot are added specified amounts of HCl and *n*-butanol and then the dithiol reagent (prep. described). The colour develops in 30 min. The liquid is then adjusted to a known vol. with *n*-butanol. The acidity of the mixture is somewhat critical and all extinctions should be measured at 20° or calibrations should be made simultaneously with sample measurements. With the difference method, the coeff. of variation is $\pm$ 0·16%. With the other procedure, concn. of Mo down to 1 p.p.m. can be determined. With

slight modification the procedure is applicable to the determination of Mo in alloys of Mo and Nb.
A. O. JONES

2124. **Use of dihydroxymaleic acid for the reduction of the molybdenum - thiocyanate complex.** N. D. Sadzhaya and L. Petruzashvili. *Trudy Tbilissk. Gos. Pedagog. Inst.*, 1957, **11**, 673–677; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,265.—Dihydroxymaleic acid (**I**) is used for the reduction of the thiocyanate complex of Mo^{VI} for the subsequent colorimetric determination of Mo. To 1 ml of the soln. of MoO_3 in water add 1 ml of 10% H_2SO_4, 0·5 ml of a 5% NH_4SCN soln. and 1 drop of a 10% soln. of $FeCl_3$ (as catalyst), and then add 5 ml of a 0·1% soln. of **I** in 60% ethanol (or the corresponding amount of crystalline **I**). Mix the soln. and after a few minutes measure the extinction with a micro-colorimeter. As little as 0·004 to 0·005 mg of Mo in 10 ml of soln. can be determined. Even smaller amounts (down to 0·002 mg of Mo in 10 ml) can be determined after preliminary extraction of the thiocyanate complex of Mo^{V} (formed by the reduction of Mo^{VI} with **I**). The extraction should be repeated several times, with amyl alcohol or butanol. The sodium salt of **I** may also be used to reduce Mo^{VI}.
C. D. KOPKIN

2125. **Analysis of nickel alloys for oxide cathodes. VII. Determination of tungsten.** G. Eckert and E. Bauersachs (Wernerwerk für Bauelemente, Siemens & Halske A.-G., Munich). *Z. anal. Chem.*, 1958, **163** (3), 161–169.—Tungsten is determined spectrophotometrically as the yellow thiocyanate complex with a strongly reduced W^{VI} soln. The reduction is performed with $TiCl_3$ after a pre-reduction with $SnCl_2$. A previous separation from Ni is unnecessary. *Procedure*—The sample of nickel alloy (25 to 50 mg) is dissolved in 1 ml of a conc. HNO_3 - conc. HCl mixture (1:5, by vol.) and the soln. is evaporated on a sand bath. The evaporation is repeated after the addition of 2 ml of conc. HCl, and the soln. of the residue in aq. NH_3 (1:1) is allowed to stand for 2 hr. The soln. is diluted to 50 ml, and to aliquots containing 50 to 200 μg of W are added 5 ml of 2 *M* $SnCl_2$ in dil. HCl (1:1), 0·2 ml of ≃ 15% $TiCl_3$ soln. and 5 ml of 2 *M* KSCN. After diluting the soln. to 50 ml, the extinction is measured in a 10-mm cell at 401 mμ (for a spectrophotometer) or 405 mμ (for an absorptiometer with mercury vapour lamp and filter) relative to water. From this value is deducted the extinction of a blank prepared from a W-free sample. The results show a standard deviation of ± 1·5%. Cobalt, Fe, Mn, Mg, Al and Si do not interfere when present in the sample at concn. < 1%. Alkali metals and alkaline-earth metals do not interfere, but Cu must not be present at concn. > 4 μg per ml in the final soln. Molybdenum and V interfere, but are not present in cathode nickel.
J. H. WATON

2126. **Use of metal-specific indicators in titrations by precipitation methods. II. Determination of the end-point in the titration of sodium tungstate with lead solution.** R. Püschel, E. Lassner and R. Scharf (Test. Lab., Metal Works, Plansee A.-G., Reutte/Tyrol, Austria). *Z. anal. Chem.*, 1958, **163** (5), 344–349.—Of the indicators tested, 4-(2-pyridylazo)resorcinol (PAR) gives excellent results with regard to the end-point detection in the titration of sodium tungstate with $Pb(NO_3)_2$ soln. It is carried out in a hexamine-buffered medium at pH 6 to 6·5 until the colour of the boiling soln. remains permanently red. Soln. containing 2 to 10 mg of W are titrated with 0·005 *M* $Pb(NO_3)_2$ and the average error is ± 0·02 mg of W.
B. B. BAUMINGER

2127. **Analytical properties of ammonium uranium pentafluoride.** E. R. Nikolaeva (School of Anal. Chem., Univ., Moscow). *Vestn. Moskov. Univ.*, 1958, (4), 193–196.—Conditions are studied for the pptn. of NH_4UF_5. This compound is completely pptd. at pH 1·5 and above with a 6 to 7-fold excess of NH_4F (calculated on the required ratio U:F = 1:5). The reduction of U^{VI} to U^{IV} with Fe^{2+} is rapid at 70° to 80°. To determine U, to 5 or 10 ml of soln. containing 0·5 to 5 mg of U add 0·5 g of $FeSO_4$, 0·2 to 0·3 g of NH_4F and dil. H_2SO_4 to pH 1·5 to 2·0. Heat at 70° or 80° for a few minutes, cool and set aside for 2 to 2·5 hr. Filter, wash the ppt. with 1·5% NH_4F soln. containing 0·25% by vol. of H_2SO_4, and dissolve it in 10 ml of 10 *N* H_2SO_4 saturated with boric acid. Titrate U with ammonium vanadate soln. No interference is caused by the presence of V, Mo and Fe in amounts < 10, 15 and 50 mg in 10 ml. The experimental error is ≯ ± 5%.
C. D. KOPKIN

2128. **Use of organic reagents in inorganic analysis. VII. Gravimetric determination of uranium with phenylglycine-o-carboxylic acid.** Sachindra Kumar Datta (Darjeeling Gov. Coll., India). *Z. anal. Chem.*, 1958, **163** (5), 349–352 (in English).—Procedures previously worked out for the gravimetric determination of Th and Zr (*cf. Anal. Abstr.*, 1958, **5**, 3302) are employed for the separation of U from Th or Zr and their determination. *Procedure*—A sample containing U and Th is neutralised to Congo red with dil. NaOH soln. and heated to boiling-point. A slight excess of 1% phenylglycine-*o*-carboxylic acid soln. (**I**) is added and, after settling for 10 min., the ppt. is filtered off, washed first with a 0·5% soln. of **I**, then hot water and ignited to ThO_2. A sample containing U and Zr is evaporated nearly to dryness, then taken up with 10 ml of glacial acetic acid, diluted to 50 ml with water and heated to boiling-point. The pptn. is carried out with 1% **I** soln., followed by 1·5 ml of 2·5% ammonium acetate soln. After settling for 10 min., the ppt. is filtered off, washed with 80% ethanol, then hot water, dried and ignited to ZrO_2. The filtrate from the Th or Zr pptn. is evaporated to 15 ml, 20 ml of conc. HNO_3 is added and the evaporation continued. After adding 20 ml of conc. H_2SO_4, the soln. is evaporated to fumes of SO_3, cooled, and extracted with H_2O, so that the concn. of H_2SO_4 in the soln. becomes 1:19. It is then passed through a Jones reductor, neutralised to Congo red paper, and cooled to 5° to 10°, and an excess of 3% **I** soln. and 10 ml of 2% ammonium acetate soln. are added. The ppt. is filtered off, washed with cold water and 50% ethanol and ignited to U_3O_8.
B. B. BAUMINGER

2129. **Micro-determination of uranium using ammonium aurintricarboxylate (aluminon) as a colorimetric reagent.** Anil K. Mukherji and Arun K. Dey (Chem. Lab., Univ. Allahabad, India). *Mikrochim. Acta*, 1958, (6), 736–743 (in English).—The 1:1 coloured chelate formed between UO_2^{2+} and aluminon has max. absorbance at 540 mμ. Tolerance limits were determined for the interferences of a large number of cations and anions. A 50-fold molar excess of the reagent is recommended, the pH maintained at 5·5 ± 0·5 and the temp. at 20° to 30°. The limit of detection of U is 10 p.p.m.
D. F. PHILLIPS

2130. **Fluorimetric determination of uranium.** T. S. Dobrolyubskaya. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 178–182; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,268.—Studies on the fluorimetric determination of small amounts of U, based on measurement of the intensity of the radiation due to U in a melt of NaF, are briefly reviewed. On the basis of the data in the literature and on the results of her own work (*Ref. Zhur., Khim.*, 1956, Abstr. No. 57,374), the author concludes that the centre of radiation in the bead is the UO_2^{2+} ion surrounded by F^- ions. Apparently the UO_2^{2+} ion replaces a Na^+ ion in the cryst. structure of NaF. The presence of F^- plays a fundamental part in the luminescence process. If instead of NaF, oxygen-containing compounds (Na_2CO_3, Na_2SiO_3) are used as the base for the preparation of melts activated by a uranium compound, irradiation of the resulting melts at 365 mμ does not produce the radiation which is characteristic of the NaF - U melts. C. D. KOPKIN

2131. **Spectrophotometric determination of uranium with 1-(2-pyridylazo)-2-naphthol.** H. H. Gill, R. F. Rolf and G. W. Armstrong (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1788–1792.—From 40 to 400 μg of U^{4+} in an aliquot of an organic extract or a soln. of an alloy or ore can be determined by extraction of $UO_2(NO_3)_2$ into a 9% (v/v) soln. of tributyl phosphate in $CHCl_3$, and then developing a colour in the organic phase by the addition of a 0·05% (w/v) methanolic soln. of 1-(2-pyridylazo)-2-naphthol (PAN) in the presence of pyridine. The extinction of the coloured complex is measured, after 15 min., at 560 mμ. Extraction of Ce^{IV} is avoided by its reduction to Ce^{III} with Fe^{II}; Th should be removed as oxalate before the extraction. Addition of EDTA (disodium salt) (0·2 g) increases the selectivity of U^{4+} extraction by complexing Zr, Bi and Mn^{3+}. The correct acidity for extraction is obtained by initial neutralisation of the sample soln. and control of the apparent pH (> 0·3) of the $Al(NO_3)_3$ used as salting soln. Analyses of soln. containing U and 37 different ions gave an average recovery of U of 99% (deviation ± 2%) by the PAN procedure, and an average recovery of 98% (deviation ± 4%) by the fluorimetric procedure. W. J. BAKER

2132. **Spectrophotometric determination of uranium with 2-(o-arsonophenylazo)chromotropic acid [Neothorin].** Hideo Matsuyama, Tadashi Hara and Kyutaro Koyama (Fac. of Engng, Doshisha Univ., Kamigyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 958–963.—Neothorin produces a violet complex with U at pH 4·9 to 6·2 in an acetate buffer, and the extinction at 600 mμ is proportional to concn. for < 15 μg per ml. Interfering ions such as SO_4^{2-} and those of Cu, Al, Ni, Co, Fe, Mo, Th and the rare-earth elements are removed by a column-extraction method (*cf.* Hara, *Anal. Abstr.*, 1957, **4**, 3942). K. SAITO

2133. **Polarographic determination of uranium.** K. Győrbiró (Inorg. Chem. Inst., Polytech. Univ., Budapest). *Magyar Kém. Lapja*, 1958, **13** (7–8), 306–308.—Methods and techniques are reviewed and applications to Hungarian ores are discussed. (12 references.) G. SZABO

2134. **Separation of uranium in chloride - nitrate medium.** M. Novák and V. Pekárek (Inst. Nucl. Physics, Prague). *Jaderná Energie*, 1958, **4** (9), 256–260.—Extraction of uranium from ore containing calcium carbonate has been studied with the use of a mixture of HCl and HNO_3 at elevated temp. The separation of uranium has been carried out by means of a strongly basic anion-exchange resin of the lutidine - formaldehyde type in the nitrate form. Uranium has been separated from the elements of the first and second group, Al, Fe, Pb, Zn and rare earths. The separation has been successful not only in a mixture of HCl and HNO_3 (adsorption capacity, 0·036 g of U per g of dry resin), but also in a medium of the corresponding Ca salt (adsorption capacity 0·256 g of U per g of dry resin). J. ZÝKA

2135. **Separation of uranium by solvent extraction into tri-*n*-octylphosphine oxide. Direct colorimetric determination with dibenzoylmethane.** C. A. Horton and J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1779–1784.—From 20 to 3000 μg of U^{6+} in the sample soln. can be determined rapidly by extraction from 3 *N* HNO_3 into an equal or double vol. of 0·1 *M* tri-*n*-octylphosphine oxide in *cyclo*hexane, followed by addition of dibenzoylmethane (0·2%, w/v) and pyridine in ethanol (5%, v/v) (≃ 10 to 25 ml) to an aliquot (1 to 3 ml) of the organic extract. The extinction of the yellow complex is measured (after ≮ 5 min.) at 405 mμ (416 mμ if V^{5+}, Ti, Zr or Th is present) in 1-cm cells with 95% ethanol as reference. Diverse interference by cations can be controlled by preliminary selective reduction (for Fe, Cr, V), fluoride complexation (in certain instances), or addition of $Al(NO_3)_3$ (for F^- or PO_4^{3-}); Cl^- interfere seriously. The standard deviation is ± 2% (30 analyses), and the range and sensitivity are greater than for Francois' method (*cf. Anal. Abstr.*, 1958, **5**, 1840). W. J. BAKER

2136. **Determination of the uranium content of ores by separation with carbonate. (Preliminary communication.)** E. Upor, L. Fekete and G. Nagy (Uranium Mine Co. of Pécs, Hungary). *Magyar Kem. Lapja*, 1958, **13** (7–8), 305.—Complete dissolution of a uranium ppt. with excess of carbonate can be achieved by adding $Th(OH)_4$, which prevents the adsorption of uranium on to the $Al(OH)_3$ and $Fe(OH)_3$ present. *Procedure*—Dissolve the ore by a suitable method, and precipitate the U with aq. NH_3 soln., after the addition of $Th(OH)_4$ (20 mg of Th per 4 mg of U). Filter, and wash the ppt. with 0·5% aq. NH_3 containing $(NH_4)_2SO_4$. Dissolve the U by washing the ppt. with hot 5% Na_2CO_3 soln. (50 to 70 ml) in small portions. Acidify with H_2SO_4 to ≃ *N* concn. Cool and reduce the U to U^{4+}, in a Jones reductor, and subsequently increase the acid concn. to 33% while cooling. Titrate with 0·005 *N* NH_4VO_3, with phenylanthranilic acid as indicator. The relative error is within ± 3%. G. SZABO

2137. **Field-chromatographic method for the determination of uranium in soils and rocks.** C. E. Thompson and H. W. Lakin. *U.S. Geol. Survey Bull.*, 1957, No. 1036-L, 209–220.—A simple chromatographic semi-quantitative determination of U, suitable for analysing soils and rocks containing 4 to 1200 p.p.m. of U, consists in mixing the ground sample with HNO_3 - $Al(NO_3)_3$ soln. and chromatographing on paper. Aq. ethyl acetate - HNO_3 is used as solvent, and the chromatograms are sprayed with $K_4Fe(CN)_6$ and evaluated by comparison with standards. CHEM. ABSTR.

2138. **Rapid polarographic procedure for the estimation of uranium in its ores.** G. V. Subbarayudu and Bh. S. V. Raghava Rao (Andhra Univ., Waltair). *J. Sci. Ind. Res., B, India*, 1958, **17** (9), 363–365.—The use of organic salts as supporting electrolytes in the polarographic assay of U in its ores is investigated. It is suggested that, for niobotantalates (non-phosphatic ores), ammonium lactate may be used and, for monazite, dil. H_2SO_4. The U contents of a number of U-containing minerals, *viz*, samarskite, allanite and monazite, are determined by this method. I. JONES

2139. **The determination of trace quantities of uranium in NRU aluminium sheathing by neutron activation analysis.** W. D. Mackintosh and R. E. Jervis (Atomic Energy Can., Ltd., Chalk River). *Atomic Energy Can., Ltd., Chalk River Project*, (481), 1957, 22 pp.—Amounts of U from 0·04 to 4·2 p.p.m. in aluminium and bauxite are determined by neutron irradiation either as ^{239}U from neutron capture or as ^{139}Ba or ^{140}Ba from ^{235}U fission. Carriers of U and Ba, respectively, are used and activities compared with standard samples. The ^{239}U method is 20 times as sensitive, although chemical operations for either method require 1 hr. CHEM. ABSTR.

2140. **Separation and determination of small amounts of rare earths in uranium.** C. V. Banks, J. A. Thompson and J. W. O'Laughlin (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1792–1795.—Milligram amounts of rare-earth elements can be separated from large concn. (≃ 1 g) of U and small concn. of Fe by adsorption of U^{VI} (sulphate) and $Fe(SCN)_3$ on a column (25 cm × 2·5 cm) of quaternary ammonium anion-exchange resin (Dowex 1-X8, sulphate form, 50 to 100 mesh). The rare-earth elements can be eluted from the resin with 0·5% H_2SO_4 and the extinction of an aliquot (≡ 100 to 200 μg of rare-earth elements) can then be measured at 570 mμ and pH 7·0 (1-cm cell) after complexation with arsenazo. The mean error is ≃ ± 1%. W. J. BAKER

2141. **The use of alkali phosphates in the analysis of uranium and thorium. The extraction of uranium with tributyl phosphate and its determination with morin.** A. Kiss and G. Almássy (Central Phys. Res. Inst., Hung. Acad. Sci., Budapest). *Magyar Kém. Foly.*, 1958, **64** (9), 332–336.—Dibutyl phosphate extracts $Th(NO_3)_4$ as a molecular compound and $UO_2(NO_3)_2$ as a complex. Tributyl phosphate (**I**) extracts both as molecular compounds, and this process is reversible. Thus, for their separation **I** must be used. *Procedure*—Evaporate the soln., which contains no anion other than NO_3^-, to dryness on a water bath. Wash the residue into a 100-ml separator with conc. HNO_3 (0·18 ml) and with water and dilute to 17 ml with water. Dissolve NH_4NO_3 (12 g) in the soln.; this increases its vol. to 25 ml. Extract it with 25 ml of a soln. of **I** in benzene (24:76) for 3 min. and remove the aq. phase. Re-extract the uranium twice with 0·2 *M* ammonium carbonate (25 ml + 5 ml) and evaporate this soln. to dryness. Transfer the residue with ethanol (15 ml) and then water (1 ml) into a 25-ml flask. Add 0·1 *N* HCl (2 ml), 1·5% EDTA (disodium salt) soln. (0·5 ml), 50% NH_4NO_3 soln. (3 ml), 0·33% morin soln. (1 ml) and make up to the mark with water. After at least 10 to 15 min., determine the extinction of the soln. in a Pulfrich photometer with an S43 filter in a 5-cm cell. The calibration curve, obtained from soln. containing various amounts of uranium, shows that the Beer - Lambert law is obeyed up to 400 μg of U. The following metals do not interfere in the amounts shown—Zr (20 μg); Mo, Th (100 μg of each); Al, Sn (200 μg of each); Fe, Co, Mg and V (300 μg of each). A. G. PETO

2142. **Separation and determination of micro amounts of uranium in the presence of thorium, bismuth and lead using the Weisz ring-oven.** P. J. Antikainen (Inst. Chem., Univ., Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (9), 277–280.—Uranium was isolated by placing a drop of the soln. on a circular filter-paper (diameter 6 cm). The paper was exposed to HF and H_2S gases to precipitate Th, Bi and Pb and held in NH_3 vapour to complete the pptn. The paper was then placed in a ring-oven (slightly > 100°) and eluted with 0·1 *N* HCl (5 to 10 drops of 0·02 ml each). After drying, the ring due to U was developed by spraying with 0·1 *M* $K_4Fe(CN)_6$ and determined by the usual Weisz procedure. The method is most suitable in the range 10 μg to 240 μg of U and has an accuracy of ≃ ± 10%. E. SJÖSTRÖM

2143. **Separation of uranium from bismuth by anion-exchange resins.** G. Banerjee and A. H. A. Heyn (Univ., Boston, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1795–1796.—Trace amounts (*e.g.*, < 50 μg) of U can be rapidly separated from a large excess of Bi^{3+} by quant. adsorption of the sulphate complex of U^{VI} on a quaternary ammonium anion-exchange resin (Dowex 1-X10, sulphate form, 100 to 200 mesh) at pH 1·0 to 1·5. The U can be eluted from the column with dil. $HClO_4$ (1:10) and then determined spectrophotometrically by the standard $NaOH - H_2O_2$ method. This procedure is particularly useful for routine analyses of liquid-metal fuel reactor samples having a wide range of Bi concn., because vol. of sample and of resin and concn. of H_2SO_4 can be easily varied. The mean error is ≃ − 0·5% (8 analyses). W. J. BAKER

2144. **Photometric determination of uranium, vanadium, molybdenum and tungsten with tannic acid.** Mitsuo Kiboku and Chozo Yoshimura (Fac. of Engng, Kinki Univ., Fuse, Osaka). *Japan Analyst*, 1958, **7** (8), 488–491.—The effect of pH on the photometric determination with tannic acid (**I**) of U (10 to 50 μg per ml) at optimum pH 6·8 and at 400 mμ, of V (7 to 30 μg) at pH 5·1 and at 620 mμ, of Mo (18 to 56 μg) at pH 5·6 and at 370 mμ, and of W (14 to 55 μg) at pH 6·8 and at 390 mμ was examined. The excess of **I** is removed by extraction with *iso*amyl alcohol. **I** is autoxidised more rapidly in a basic soln. than in an acid soln.; deteriorated soln. recovers its original transmission by shaking with zinc amalgam in 2 *N* H_2SO_4. K. SAITO

2145. **Nuclear emulsion technique for determination of the plutonium-240 - plutonium-239 ratio.** E. N. Sloth and M. H. Studier (Argonne Nat. Lab., Lemont, Ill.). *Anal. Chem.*, 1958, **30** (11), 1751–1753.—In ^{240}Pu, 24·28% of the α-particles emitted have coincident electrons arising from γ-ray conversion, but for ^{239}Pu this fraction is 11·32%; the specific activity of ^{240}Pu is four times that of ^{239}Pu. Incorporation of the activity in an Ilford G-5 nuclear track emulsion (with long exposure if required) and scanning of the plate with a microscope permit determination of the isotope ratio at

the level of one disintegration per min. (10^{-11} g of Pu as nitrate in 0·01 *N* ammonium acetate at pH 5 to 6). The accuracy is limited by the statistics of track counting, and for 3 to 5% of ^{240}Pu the standard deviation, based on 10^4 events, is 40% to 30%. Activity from ^{238}Pu interferes and a correction is applied after determination of ^{238}Pu content with a pulse height analyser.

J. P. STERN

2146. **Low-level plutonium-241 analysis by liquid scintillation techniques.** D. L. Horrocks and M. H. Studier (Argonne Nat. Lab., Lemont, Ill.). *Anal. Chem.*, 1958, **30** (11), 1747–1750.—To determine the very small amounts of ^{241}Pu in plutonium, the light pulses produced by the β-particles derived from ^{241}Pu (as dibutyl phosphate) in an organic scintillating soln. were measured with a slightly modified commercial coincidence-type liquid scintillation spectrometer. The method eliminates losses of the low-energy (< 18 keV) β-rays and permits simplification of sample prep. With a low-energy cut-off at 4 keV, counting efficiency is 36 to 38%. The α-emitting ^{238}Pu, ^{239}Pu and ^{240}Pu do not interfere, and the α-particles may be counted separately with 100% efficiency. Dibutyl phosphate does not affect the light output. The method permits detection of 10^{-15} g of ^{241}Pu and ready recovery of Pu; it is thus preferred to techniques in which internal proportional counters are used.

J. P. STERN

2147. **Determination of americium in plutonium by gamma counting.** J. Bubernak, M. S. Lew and G. M. Matlack (Univ. of Calif., Los Alamos, N. Mex.). *Anal. Chem.*, 1958, **30** (11), 1759–1762.—The γ-ray specific activity (for rays above 30 keV) of ^{241}Am (main peak at 59·6 keV) is 3×10^4 times that of ^{239}Pu (which has largely *L* X-ray activity). A suitable sample is counted for α-activity, giving the Pu content, and then for γ-activity (in a well-type scintillation detector with discriminator at 30 keV); this value is corrected for the contribution by Pu and the Am activity thus obtained. The method permits determination of 5 p.p.m. of Am in plutonium and is accurate to within $\pm$ 2% for 5×10^{-7} g of Am.

J. P. STERN

2148. **Mercurimetric titrations with redox indicators. I. Determination of halides and mercuric ions.** J. Bognár and O. Jellinek (Tech. Univ. for the Heavy Indust., Miskolc, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **17** (1), 17–26.—This is an English translation of the paper abstracted in *Anal. Abstr.*, 1958, **5**, 2623.

2149. **Determination of trace amounts of mixed halides [in phosphors] by activation analysis.** J. F. Cosgrove, R. P. Bastian and G. H. Morrison (Sylvania Electric Products Inc., Bayside, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1872–1874.—Concn. as low as 0·001 μg of Br and 1 μg of Cl or I in zinc sulphide can be determined to within $\pm$ 3·5% by a neutron-activation method. The sample (0·5 to 1 g) is irradiated for 24 hr. at a flux of $3{\cdot}4 \times 10^{12}$ neutrons per sq. cm per sec. The activated zinc sulphide is then dissolved in dil. HNO_3 (containing 20 mg of each of the halides as carriers), and ^{128}I and ^{82}Br are separated by solvent extraction and ^{38}Cl by distillation. An analytical procedure for completing this separation in $\simeq$ 1 hr. is given. The activity of each radiochemically pure halide is measured by β-counting ($< 10^4$ counts) and is compared with the activity of each standard halide soln. The limits of sensitivity are valid provided that > 3 hr. elapse between the time of removal from the pile and the completion of the chemical separation. Secondary reactions during irradiation interfere, *e.g.*, $^{32}S \rightarrow {}^{35}Cl$ and $^{80}Se \rightarrow {}^{82}Br$, so that it may be necessary to resolve the complex decay-curve of the Br fraction.

W. J. BAKER

2150. **Volumetric - gravimetric method for the mercurimetric determination of chloride ion.** V. V. Evdokimov. *Uch. Zap. Kazansk. Univ.*, 1957, **117** (9), 201–203; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,326.—The accuracy of the mercurimetric determination of Cl^- (*Ref. Zhur., Khim.*, 1956, 47,227) in a pure soln. of NaCl is studied. The determinable minimum when titrating with 0·05 *N* $Hg_3(NO_3)_2$, with the addition of 1 drop of a soln. of diphenylcarbazone as indicator before reaching the end-point, is 5×10^{-5} g of Cl^-. The coeff. of variation varies according to the concn. of Cl^- from $\pm$ 0·1% to $\pm$ 2%.

C. D. KOPKIN

2151. **Hydrazinometric determination of bromate and oxalate ions.** L. Szekeres, L. G. Molnár and M. Nagy (Chem. Inst., Agric. Univ., Budapest). *Magyar Kém. Lapja*, 1958, **13** (7–8), 302–303.—A 0·1 *N* soln. of hydrazine sulphate (**I**), previously recryst. and dried at 130°, is stable and can be used for a determination of BrO_3^- with Br^- and iodine - starch indicator. *Procedure for bromate*—To an approx. 0·1 *N* $KBrO_3$ soln. (10 ml) in a Buchböck bromination flask are added 0·15 g of KBr and 10 ml of 2 *N* HCl. The liberated Br is titrated with **I** soln. Near the end-point, one drop of 0·1 *N* iodine and 1 ml of starch soln. are added and titrated to a permanent blue colour. *Procedure for oxalate*—A 0·1 *N* $KBrO_3$ - KBr soln. (2·7836 g of $KBrO_3$ and 15 g of KBr diluted to 1 litre) (10 ml) is diluted with 10 ml of H_2O in a Buchböck flask, and 10 ml of 2 *N* HCl is added. A few minutes later the liberated Br is converted into NaOBr with 6·5 ml of 5 *N* NaOH. A 5-ml aliquot of the sample ($\simeq$ 0·1 *N* oxalate) is added and the soln. is diluted with 10 ml of H_2O and 5 ml of 50% acetic acid. After 30 min., 5 ml of conc. HCl is added and after a further 20 min. the excess of Br is titrated with **I**, two drops of 0·1 *N* KI and 1 ml of starch soln. being used as indicator. Results are accurate to within $\pm$ 0·2%.

G. SZABO

2152. **The polarographic determination of small quantities of iodine in iodised salt.** V. Pliška and D. Rykl (Dept. Chem. of Food, School of Chem., Prague). *Československ. Farm.*, 1958, **7** (9), 515–516.—This method is a modification of the procedure suggested by Novák (*Chem. Listy*, 1953, **47**, 903) in which iodide is oxidised with hypobromite to iodate and the latter is determined polarographically. The modified method can be used even with extremely low contents of iodine (*e.g.*, for salt or brines). *Procedure*—Dissolve the salt (10 g) in H_2O (35 ml), and add a standard soln. of KI (0·005%) (1 ml). Make the soln. alkaline with *N* NaOH (1 drop) and mix with sodium hypobromite (2·5 ml) [to satd. bromine water (50 ml) add 20% NaOH soln. until the mixture is faintly green]. The excess of hypobromite is removed after 5 min. by adding a satd. soln. of Na_2SO_3 (1·5 ml). Add 25% aq. NH_3 (0·8 ml) and 0·001 *M* $CdSO_4$ (5 ml). Add gelatin soln. (0·5%, 1 ml), make up to 50 ml with H_2O and record the polarographic curve. Evaluate by the use of Cd^{2+} as pilot ion. An accuracy of $\pm$ 6% for $\simeq$ 0·1 mg of iodine in 1000 g of salt is claimed.

J. VOLKE

2153. **Iodimetric assays. V. Determination of mixtures of iodate and periodate.** L. Szekeres, M. Rády and E. Kardos (Chem. Inst., Agric. Univ., Budapest). *Magyar Kém. Lapja*, 1958, **13** (7–8), 303–304.—Periodate ions are converted mainly into iodate and partly to iodine by reduction with HBr. On being made alkaline, the iodine is oxidised to iodate by the hypobromite present. The excess of hypobromite is reduced with H_2O_2 and the latter decomposed by heating. *Procedure*—Potassium bromide (0·5 to 1·0 g) and 5 to 12·5 ml of 2 *N* HCl are added to 10 to 25 ml of an $\simeq$ 0·1 *N* soln. of IO_3^- and IO_4^-. The soln. is neutralised with 2 *N* NaOH after 3 to 10 min., and 2 to 5 g of $NaHCO_3$ and 10 to 25 ml of a 3% H_2O_2 soln. are added and the mixture is heated on a water bath for 15 min. It is then diluted and acidified with 20% HCl and, after addition of 10 to 25 ml of 2% KI soln., is titrated with 0·1 *N* $Na_2S_2O_3$ to give the value for IO_3^- and IO_4^-. Another aliquot is iodimetrically titrated directly to give the value for IO_4^-, and both ions can then be calculated. Data are tabulated for various mixtures. G. Szabo

2154. **Amperometric titration of manganese.** H. Grubitsch and B. R. Nilsen (Inst. of Technol. for Inorg. and Anal. Chem., Graz, Austria). *Z. anal. Chem.*, 1958, **163** (5), 353–359.—Three methods have been tested and found to give fairly satisfactory results. The authors describe procedures by Volhard - Wolff and Lingane - Karplus, and in both cases the titration is carried out in 5 min. with a relative error of $\pm$ 0·1%. B. B. Bauminger

2155. **Analysis of solutions containing manganese ions of various valencies.** E. S. Dzhaparidze and D. A. Gorgishvili. *Soobschch. Akad. Nauk GruzSSR*, 1957, **19** (4), 407–414; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,273.—Methods are evolved for the determination of ions of Mn of various valencies when present together in soln. (Mn^{3+} - Mn^{4+}, MnO_4^- - MnO_4^{3-}, Mn^{3+} - Mn^{4+}). For the analysis of a mixture of Mn^{3+} and Mn^{4+}, first determine Mn^{3+} in one portion of the test soln. by titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$, and then determine Mn^{2+} in another portion by potentiometric titration against $KMnO_4$ in a pyrophosphate medium. The presence of Mn^{3+} in the soln. does not affect the titration of Mn^{2+}, since the latter is oxidised to Mn^{3+}, forming the stable complex $[Mn(H_2P_2O_7)_3]^{3-}$. For the analysis of a mixture of MnO_4^- and MnO_4^{3-}, use a procedure based on measurement of the oxidative capacity of the mixture MnO_4^- - MnO_4^{3-} and the oxidative capacity of the same mixture after conversion of MnO_4^- to MnO_4^{3-}. The second step of the analysis can be completed by calculation, without using special reagents which react with MnO_4^- or MnO_4^{3-}, by determining total Mn and multiplying the result by the appropriate conversion factors to obtain the oxidative capacity in terms of MnO_4^{3-}, MnO_4^- or MnO_2. The determination of Mn^{3+} and Mn^{4+} when present together is carried out in the same way as for the mixture of MnO_4^- and MnO_4^{3-}. In one portion of the soln. determine total Mn^{3+} and Mn^{4+} by titration with $(NH_4)_2SO_4.FeSO_4.6H_2O$ in acid medium containing $Na_4P_2O_7$, and then determine total Mn after reduction of Mn^{4+} with $(NH_4)_2SO_4.FeSO_4.6H_2O$ in acid pyrophosphate medium. The described methods gave satisfactory results in the analysis of synthetic mixtures containing the indicated pairs of ions in various proportions. C. D. Kopkin

2156. **New rapid method for the gravimetric determination of iron.** J. Dick (Inst. Politeh., Timişoara, Romania). *Acad. R.P.R., Baza Cercet. Ştiinţ. Timişoara, Stud. Cercet. Ştiinţ., Ser. I.*, 1957, **4**, 47–54.—This method is based on the formation of a double complex of phenazone and thiocyanate with Fe $[Fe(C_{11}H_{12}N_2O)_3(SCN)_3]$. To 5 g of $FeCl_3$ in 500 ml of water add, in order, 50 g of NH_4SCN, 5 ml of acetic acid and 40 g of phenazone dissolved in 100 ml of water. Stir the soln. vigorously until a red flocculent ppt. is formed. Heat the soln. to 50° to 60° with continuous stirring until the ppt. floats then allow it to stand for 2 hr., stirring occasionally; during this time the ppt. is deposited at the bottom in a cryst. mass. Collect the ppt. in a Buchner funnel and wash it 10 to 12 times with a soln. containing 2% of NH_4SCN, 1% of phenazone and 1% of acetic acid, and then 5 times with a soln. containing 0·02% of NH_4SCN, 0·01% of phenazone and 0·01% of acetic acid. The ppt. is dried at 100°. It is insol. in water and ether, but is sol. in acetone. As little as 0·2 μg of Fe or 0·0008 mg of Fe per ml can be detected. The average deviation is $<$ $\pm$ 0·05%. Iron can be determined by this method in the presence of Si, Al, Cr, Ti, Mn, Co, Ni, Ba, Ca, Mg, Bi, Cd, Ag, Hg, Sb, As and the alkali metals, but not Zn, Cu or Sn. Chem. Abstr.

2157. **Spectrophotometric determination of iron with chromotropic acid.** L. Sommer (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (8), 1485–1500.—*Detection*—To a drop of the acid soln. of the sample (pH 1) add a crystal of chromotropic acid or its disodium salt and a few crystals of hexamine and mix. In the presence of Fe^{3+}, a blue - green or green colour appears (pD = 5·0); interference is caused by PO_4^{3-}, F^-, and large amounts of hydroxy acids and of oxalic acid. *Photometric determination*—To an acid soln. of Fe^{3+} (1 to 16 μg of Fe in 1 ml) add a soln. of the disodium salt of chromotropic acid (1%) (10 ml), hexamine buffer soln. (70·1 g of hexamine and 5 ml of *N* HCl in 500 ml of H_2O) (10 ml), a few drops of aq. NH_3 (1 : 1) and adjust the pH to between 6·8 and 7·5 and the vol. to 50 ml. After 40 min. measure the extinction at 640 mμ. The addition of $K_2S_2O_4$ soln. (2%) (5 ml) prevents the oxidation of chromotropic acid with Fe^{3+}. Large amounts of F^-, PO_4^{3-}, organic hydroxy acids, oxalic acid, Al, Be, UO_2^{2+}, Ti^{4+}, VO_3^-, WO_4^-, Zr^{4+} and MoO_4^{2-} interfere. J. Zýka

2158. **Influence of certain elements on the intensity of the spectral lines of iron.** A. M. Kripskil. *Dokl. Akad. Nauk BSSR*, 1958, **2** (1), 11–14; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,674.—Results are given of the study of the mutual influence of Fe and S, Si, C, Mg, Al, Zn, Pb, Sn, Mn, Ni, Cr, W, Cu, Ce and Zr. The spectra were photographed in a medium spectrograph, with excitation in an a.c. arc and low-voltage and high-voltage sparks. Nickel has the least influence on the lines of Fe, and the intensity of the iron lines using iron and nickel electrodes is taken as unity. The greatest increase in the intensity of the iron lines (1·2 to 5 times) is found with S, and smaller increases with C, Si, Mg, Al, Zn, Sn, Pb and Mn. The remaining elements have an insignificant influence. In the least vigorous conditions of the arc the strengthening of the iron lines is not observed, but the influence reaches a max. in the low-voltage spark discharge, decreasing in the condensed discharge. The introduction into the discharge of small concn. of these elements ($<$ 1%) has no influence on the intensity.

The reverse effect is also observed: there is a weakening of the lines of the elements on introducing Fe into the discharge, reaching a max. in the low-voltage spark. The change in the intensity of the lines is not entirely explained by the change of temp. of the plasma and the manner of introduction of the substance into the discharge. In the discharge cloud the excitation energy is apparently transferred to the atoms of Fe from the elements indicated by collisions of the second order.

C. D. KOPKIN

2159. **Determination of small amounts of silicon in high-purity iron.** H. G. Short and A. I. Williams (National Phys. Lab., Teddington, Middx., England). *Analyst*, 1958, **83**, 624–627.—The soln. of the sample (1·5 g) in dil. H_2SO_4 is filtered and insol. matter is reserved for determination of insol. SiO_2. The filtrate is warmed with H_2O_2, maintained at near b.p. for 10 min., cooled and adjusted to a known vol. Ammonium molybdate soln. is added to an aliquot and the liquid is set aside for 15 min. at 20° ± 2°. Oxalic acid and $FeSO_4$ soln. are then added and the liquid is again set aside for 10 min. To a similar aliquot the same vol. of oxalic acid, ammonium molybdate soln. and $FeSO_4$ soln. are added, but in this order. The difference in the extinctions of the two liquids is measured in a Spekker absorptiometer and referred to a standard graph. Insol. SiO_2 is determined similarly after fusion with fusion mixture and solution of the melt in dil. H_2SO_4. In an activation procedure, the soln. in acid of the irradiated sample is evaporated to dryness with a sodium silicate carrier, the soln. of the residue in HCl is centrifuged, the SiO_2 is collected, ignited and fused with Na_2WO_4 and Na_2CO_3 and the melt is dissolved in water. After purification of the extract with a series of pptn. with carrier soln. the liquid is evaporated, the residue is treated with HCl, and the SiO_2 is collected, counted and, to determine the yield, ignited and weighed.

A. O. JONES

2160. **Photometric determination of boron in iron after decomposition by fusion with sodium peroxide.** Z. Večeřa and B. Bieber (Res. Inst. of Materials and Technology, Brno, Czechoslovakia). *Hutn. Listy*, 1958, **13** (9), 808–811.—The sample is decomposed by fusion with Na_2O_2, and B is determined photometrically with quinalizarin as reagent. The method can be carried out within 2 to 3 hr. and is suitable for samples containing 0·002 to 0·01% of B. The accuracy is within ± 0·0002%. *Procedure*—Filings of the sample (0·5 g) and Na_2O_2 (3 g) are mixed and fused in a nickel crucible. The product is cooled, heated with H_2O (30 to 40 ml), saturated with a stream of CO_2 (15 min.) and heated again with $FeSO_4$ (0·5 to 1 g). The contents of the crucible are filtered through a paper filter into a nickel or platinum dish. The ppt. is washed with Na_2CO_3 soln. (1%) (5 to 6 ml) and with H_2O. The filtrate is evaporated, cooled, dissolved in H_2SO_4 (1 + 1) (10 ml), transferred quant. to a 25-ml flask and diluted to volume. A 4-ml aliquot is transferred to another 25-ml flask, a small amount of hydrazine sulphate, conc. H_2SO_4 (15 ml) and the soln. of quinalizarin (0·01 g in 100 ml of conc. H_2SO_4) (2 ml) are added and the soln. is diluted to volume with conc. H_2SO_4. The extinction is measured after 30 min. with the use of an S61 filter and compared with a calibration curve.

J. ZÝKA

2161. **General scheme for examination of precipitates and inclusions in steel.** G. R. Booker and J. Norbury (Richard Thomas & Baldwins, Ltd., Aylesbury, Bucks.). *Brit. J. Appl. Phys.*, 1958, **9** (9), 361–365.—A scheme is described for examination of included materials in steel by electron microscopy and diffraction, X-ray diffraction and fluorescence, and spectroscopy. The scheme enables the precise form and identity of the included materials to be determined with small specimens and has been applied to iron and alloy carbides and nitrides, oxides and sulphides present in steel.

C. H. COWPER-COLES

2162. **Simplified equipment for determining hydrogen in steel.** E. Marianeschi and R. Coletti. *Metallurg. Ital.*, 1957, **49**, 673–676.—The method described is a variant of the classical method of vacuum extraction at 650°. Usually the H extracted from the sample is compressed in a McLeod or Töpler apparatus and then measured. In the method proposed, the amount extracted from the sample is measured by the variation in pressure in the constant-vol. extraction chamber when degassing the sample. A Pirani vacuum-meter with bridge circuit calibrated in ml of H is used.

IRON AND STEEL INST. ABSTR.

2163. **Determination of traces of zinc in ferrous metals.** J. Migeon (IRSID, St.-Germain-en-Laye, France). *Chim. Anal.*, 1958, **40** (8), 287–292.—A polarographic method is given for small quantities (≃ 0·001 to 0·01%) of Zn in steel. The sample is dissolved in HNO_3 (1 : 1), and Fe and Mn are removed by pptn. with aq. NH_3, NH_4Cl and $(NH_4)_2S_2O_8$. Copper is removed by electrolysis followed by dithizone extraction in acid soln. (0·1 *N* HCl) to remove final traces. Zinc is isolated from this soln. by double extraction with dithizone at pH 5·5 after the addition of KCN. It is then re-extracted with 0·02 *N* HCl, organic matter is destroyed with $HClO_4$ and H_2SO_4, and finally the Zn is determined polarographically in an aq. NH_3 - NH_4Cl soln. containing gelatin. The method is illustrated by reference to its use for the analysis of steel samples containing Mn, Ni, Cu and Co.

W. T. CARTER

2164. **Colorimetric determination of aluminium in steel with Solochrome cyanine R.** P. H. Scholes and D. V. Smith [Metallurgy (General) Div. Lab., B.I.S.R.A., Hoyle St., Sheffield, England]. *Analyst*, 1958, **83**, 615–623.—The sample (1 g) is dissolved in dil. H_2SO_4 and if the SiO_2 content is > 1% the soln. is evaporated to fuming-point, diluted and filtered through paper pulp. The insol. residue is ignited, treated with HF and H_2SO_4, heated to ≃ 800°, fused with $NaHSO_4$ and, unless the acid-insol. fraction is to be determined separately, the aq. soln. of the melt is added to the main filtrate. The liquid is electrolysed under specified conditions with a mercury cathode to remove Fe and Cr and the electrolyte is filtered. The filtrate reduced by evaporation to ≃ 5 ml is poured slowly into 10 ml of 0·1 *N* NaOH in a stainless-steel beaker. The liquid is boiled gently after cautious addition of H_2O_2, paper floc is added and after 5 min. the soln. is filtered, neutralised and made slightly acid. A 10-ml aliquot (≡ 2 to 70 μg of Al) is treated with exactly 5 ml of a 0·1% aq. soln. of Solochrome cyanine R and an acetic acid - acetate buffer soln. (pH 6·1). The vol. is adjusted to 100 ml and after 30 min. the extinction is measured against a reagent blank at 535 mμ, or in an absorptiometer, and referred to the extinctions of calibration soln. The precision is ± 0·001%.

A. O. JONES

2165. **Apparatus for determining combined carbon in steel and cast iron by selective oxidation - reduction.** F. Marion (Lab. de Prof. Faivre, Fac. des Sci., Nancy, France). *Bull. Soc. Chim. France*, 1958, (8–9), 1187–1188.—The hydrocarbon gases produced by selective oxidation - reduction (*cf. Anal. Abstr.*, 1959, **6**, 1740) are oxidised to CO_2 and absorbed in $Ba(OH)_2$ soln. *Procedure*—Gas from a cylinder containing N and H (1 : 1) is passed through a column of KOH, over copper at a red heat, through a bubbler containing $Ba(OH)_2$ and into a vessel of water heated in a thermostat to give a constant v.p. of water, and thence over the sample of steel or iron heated to 700°. The hydrocarbons are carried over into a tube packed with CuO heated at 930° to 950°. The CO_2 formed is absorbed in standard $Ba(OH)_2$ soln., which is back-titrated with standard acid. The reaction is complete in $\simeq$ 4 hr. The results agree with those from the method of determining total carbon in the sample after passage of H, and in an untreated sample. This method gives a better result when the amount of combined C is low. E. J. H. Birch

2166. **Colorimetric determination of silicon in iron and steel.** W. B. Sobers (Chain Belt Co., Milwaukee, Wis., U.S.A.). *Foundry*, 1957, **85** (10), 234–240.—The procedure is a modification and simplification of the colorimetric method of Haywood and Wood ("Metallurgical Analysis by Means of the Spekker Photo-Electric Absorptiometer," 1944). The determination takes about 40 min. and the method is accurate to within 0·02%. *Procedure A*—Dissolve a 200-mg sample in 10 ml of 25% H_2SO_4 (**I**) and 40 ml of H_2O, add 6 ml of 2·5% $KMnO_4$ soln. (**II**), boil for 3 min. and reduce the soln. with a slight excess of 10% Na_2SO_3 soln. (**III**). Boil off excess of SO_2, transfer the soln. to a 200-ml flask and dilute to the mark (1 ml ≡ 1 mg). For the blank test add the following reagents to a 20-ml aliquot—40 ml of H_2O, 20 ml of **I**, 10 ml of 5% ammonium molybdate soln. (**IV**) and 10 ml of 1% $SnCl_2$ soln. (**V**). For the sample test, to another 20-ml aliquot add 30 ml of H_2O and 10 ml of **IV**, set aside for 5 min. and add 20 ml of **I** and 10 ml of **V**. Dilute to 100 ml with water. Allow each soln. to stand at least 20 min. before reading. Compare at 650 mμ by using the blank sample as reference. The curve is plotted by using standard steel samples of known silicon content. *Procedure B*—Apply if there is a limited amount of sample available. Dissolve a 40-mg sample with 20 ml of 2% H_2SO_4, dilute to 30 ml, boil, and add several drops of **II**, boil for 3 min., and reduce with several drops of **III**. Boil off the excess of SO_2, dilute to 75 ml, and transfer to a 100-ml flask and dilute to the mark. Transfer 50 ml of this to the original beaker, add 10 ml of H_2O, and treat as outlined under *A* for a blank soln.; use the remaining 50 ml for sample soln. as shown in *A*. *Procedure C*—Use for determining Si in higher silicon irons. For material containing 0·60 to 1·20% of Si use a 200-mg sample and proceed as outlined under *A* with the exception that only two 10-ml aliquots are used. Apply the same curve and multiply the results by 2. For iron containing from 1·20 to 2·5% of Si use a 100-mg sample and proceed as shown in *A* with the exception that 3 ml of **II** is used for oxidation and two 10-ml aliquots are taken. Apply the same curve and multiply the results by 4. Chem. Abstr.

2167. **Volumetric determination of silicon in ferrosilicochrome.** S. Král and J. Sedlář (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1958, **13** (9), 812.—*Procedure*—Into a platinum crucible weigh the finely powdered sample (0·2 g), add HNO_3 (1 : 1) (20 ml) and HF (8 ml). Cover the crucible with a filter moistened with KNO_3 soln. Allow the sample to dissolve while cooling, transfer the filter to the crucible, add KNO_3 (12 g) and filter after 15 min. Wash with KNO_3 soln. (20%) till the filtrate becomes alkaline, transfer the ppt. with the filter into a beaker, add hot H_2O (100 ml) and titrate with 0·4 *N* NaOH to phenolphthalein.

J. Zýka

2168. **Determination of oxide inclusions in carbon steel.** A. Šmrhová, L. Brháček and J. Janáček (VŽKG, Ostrava, Czechoslovakia). *Hutn. Listy*, 1958, **13** (3), 253–257.—*Procedure*—After separating the inclusions by means of chlorination and vacuum sublimation, ignite them in a platinum crucible, transfer to a beaker and remove colloidal SiO_2 by heating for 2 min. with 3% Na_2CO_3 soln. Filter off and wash the ppt. with hot H_2O (× 3), 0·5% Na citrate soln. (× 2) and cold H_2O (× 5). Ignite the filter in a platinum crucible and weigh. Decompose the residue by heating with conc. HCl (3 ml) and H_2SO_4 (1 : 1) (1 ml), evaporate and weigh ($CaSO_4$). Determine SiO_2 gravimetrically after evaporating with a mixture (1 : 1) of conc. HF and H_2SO_4. Fuse the residue with $K_2S_2O_8$ (1·5 g), wash with H_2O, add H_2SO_4 (3 drops) and dilute to vol. Determine Mn colorimetrically in a suitable portion of this soln. after oxidation with $(NH_4)_2S_2O_8$ and $AgNO_3$. Oxidise another portion with H_2O_2 and determine Fe by titrating with 0·002 *M* EDTA (disodium salt) (**I**), in ammonium acetate buffer soln. (pH 2) at 40° to 50° (salicylic acid as indicator). Then add an excess of **I**, adjust the pH to 5, boil and titrate the soln. at 70° with 0·002 *M* $FeCl_3$ till pink (Al plus Fe). In another part of the soln. determine Cr amperometrically with $FeSO_4$ soln. after oxidation with $(NH_4)_2S_2O_8$ and $AgNO_3$ (MnO_4^- are reduced with NaCl soln.). Determine Cu polarographically in NH_4Cl soln (Cr^{VI} must be reduced with Na_2SO_3). Calcium can be determined complexometrically in the usual way (buffer soln. pH 10, Eriochrome black T as indicator). Lower contents of Si (< 15%) must be determined colorimetrically after conversion into molybdosilicate. J. Zýka

2169. **The micro-analysis of oxide inclusions in steel. Determination of silica, alumina, iron oxide and manganese oxide.** S. Meyer and O. G. Koch (Hauptlab. der Neunkircher Eisenwerk A.-G., Neunkirchen/Saar, Germany). *Mikrochim. Acta*, 1958, (6), 744–755.—Weigh 200 to 400 μg of the sample in a platinum crucible. Determine SiO_2 by difference after fuming with $HClO_4$ - HF. After fusion of the residue with Na_2CO_3 - K_2CO_3 - $Na_2B_4O_7$ and dissolution of the melt, separate Fe by extraction with diethyl ether and determine photometrically with 1 : 10-phenanthroline. Extract Al with 8-hydroxyquinoline - $CHCl_3$ and determine photometrically. Finally extract Mn with Na diethyldithiocarbamate - $CHCl_3$ and determine photometrically. One analyst can complete four samples in 6 to 8 hr. and further time-saving is possible by the provision of suitable apparatus. The relative error varies from ± 5 to ± 10%.

D. F. Phillips

2170. **Determination of vanadium in high-chrome steel.** A. S. Vernidub and V. I. Petrashen'. *Trudy Novocherk. Politekh. Inst.*, 1958, **69–83**, 149–152; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,712.—The chromatographic separation of V and Cr by

means of the thiocyanate complex of Cr is used in the analysis of high-chrome steel containing 0·02 to 0·24% of V. Dissolve 0·5 to 1 g of sample by boiling with 40 ml of H_2SO_4 (1:4) for 15 to 20 min., add a few drops of HNO_3 (1:1), evaporate to fumes of SO_3, cool, add 1 to 1·5 ml of H_2SO_4 (1:4) and 25 ml of 4 *N* KSCN (giving a total vol. $\geq$ 170 ml), boil for 2 or 3 min., cool and adsorb the V on the cationite SBS (NH_4^+ form), which has been freed from traces of Fe^{3+} by washing with 0·5 *N* H_2SO_4. The passage of the soln. takes 2·5 to 3 min. Wash the cationite with water till the wash soln. shows a negative reaction for SCN^- and elute V with 300 ml of H_2SO_4 (1:8). Then pass 20 to 30 ml of water through the column at the same rate, followed by a rapid stream of 100 to 150 ml of water. Make the soln. up to 500 ml. To a 50-ml aliquot add 0·1 *N* $KMnO_4$ dropwise to a stable pink colour, 50 ml of water, a few drops of 0·1 *N* $NaNO_2$ to a colourless or slightly green colour and a further 3 drops (to destroy excess of $KMnO_4$). Immediately add $\simeq$ 1 g of urea, shake for 1 or 2 min., add 8 to 10 ml of H_2SO_4 (1:4) and titrate with 0·008 *M* $(NH_4)_2SO_4.FeSO_4.6H_2O$ potentiometrically, or visually after adding N-phenylanthranilic acid as indicator and allowing to stand for 1 to 2 min. The error in determining 0·02% of V is $\pm$ 5%, and in determining 0·24% of V is $\pm$ 3%.

C. D. KOPKIN

2171. **Determination of tungsten in steel not containing niobium and tantalum.** B.I.S.R.A. Methods of Analysis Committee. *J. Iron St. Inst.*, 1958, **190** (1), 51–55.—A gravimetric method is recommended for tungsten contents of 3 to 32%.

J. W. O. PYEMONT

2172. **New rapid method for the gravimetric determination of cobalt.** J. Dick and F. Mihai. (Inst. Politeh., Timişoara, Romania). *Acad. R.P.R., Baza Cercet. Ştiinţ. Timişoara, Stud. Cercet. Ştiinţ., Ser. I*, 1957, **4**, 73–77.—Cobalt is pptd. as the diluturate of formula $(C_4H_3O_2N_4NO_2)_2Co.8H_2O$. The determination is carried out by dissolving 0·1 to 0·2 g of sample in 50 to 80 ml of water, adding 20 to 30 ml of 2% diluturic acid soln. in 40% ethanol and stirring. The soln. is decanted through a glass or porcelain crucible, washed 5 to 6 times with 30% ethanol, 5 to 6 times with 3 ml of 95% ethanol, and finally 4 to 5 times with absolute ethanol. The ppt. is dried in a vacuum-desiccator for 5 min. Nickel, Cu, Cd, Pb and Zn interfere. The sensitivity is 5 μg of Co per ml. CHEM. ABSTR.

2173. **Spectrophotometric determination of cobalt and iron with sodium 2-nitroso-1-naphthol-4-sulphonate.** V. N. Tolmachev and L. N. Serpukhova. *Trudÿ Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 115–124; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,277.—The method for determining comparable amounts of Co and Fe when present together by the use of Na 2-nitroso-1-naphthol-4-sulphonate (**I**) comprises photometry of soln. of the complexes of the metals with **I** at 660 mμ (only the iron complex absorbs) and at 520 mμ (both complexes absorb). It is established that with excess of **I** both Fe^{2+} and Fe^{3+} apparently form the same coloured compound; when determining Fe as Fe^{3+} with excess of **I** no reduction is necessary. The method described can be applied to the determination of Fe and Co in the presence of comparable amounts of Ni and Cu; a pH $<$ 2 must be used.

C. D. KOPKIN

2174. **The analytical chemistry of the pyridine thiocyanates. I. Separation of cobalt and nickel by solvent extraction.** J. H. W. Forsythe, R. J. Magee and C. L. Wilson (Chem. Dept., The Queen's Univ., Belfast, N. Ireland). *Talanta*, 1958, **1** (3), 249–251.—Cobalt and Ni readily form pyridine thiocyanates which are extracted with organic solvents and determined absorptiometrically. *Procedure*—Add 0·5 ml (excess) of 40% KSCN soln. to 20 ml of a soln. containing $\leq$ 50 μg of Co and $\leq$ 100 μg of Ni. Add HCl to give a pH of 2·5 to 3·0 and adjust to pH 4·6 by slow addition of pyridine; extract the ppt. of the nickel complex with $CHCl_3$ (2 $\times$ 10 ml) and make the extract up to 25 ml. Filter, and read the extinction at 320 mμ. To the aq. layer add HCl to a pH of 2·5 to 3·0, then pyridine slowly to pH 5·6 and extract the cobalt ppt. with *iso*butyl methyl ketone (2 $\times$ 10 ml). Filter and read the extinction at 620 mμ.

P. D. PARR-RICHARD

2175. **Ion-exchange analysis of nickel matte.** Masuo Kojima and Akira Iguchi (College of Gen. Educ., Tokyo Univ., Meguro-ku). *Japan Analyst*, 1958, **7** (8), 514–516.—When a 3 *N* HCl soln. of nickel matte is added to a column (diam. 1 cm, length 5 cm) of Dowex 1-X8 (Cl^-) (100 mesh), Co ($<$ 1%) and Fe ($\simeq$ 50%) are adsorbed and Ni ($\simeq$ 25%) passes through with SO_4^{2-} (5 to 15% of S) and PO_4^{3-} ($\simeq$ 10% of P). Cobalt and Fe are eluted with HCl [(4 *N*) (40 ml) and (0·1 *N*) (40 ml), respectively]. Nickel in the first eluate is adsorbed on Amberlite IR-120 (H) and separated from SO_4^{2-} and PO_4^{3-}. The metals are titrated with EDTA by the usual method, and SO_4^{2-} and PO_4^{3-} are differentially titrated with NaOH (0·05 *N*), with bromothymol blue (0·1%) and phenolphthalein (0·1%) as indicators. The sample (100 mesh) is dissolved in a mixture of HCl and HNO_3 (1 + 3, by vol.) and aq. Br soln., and evaporated to dryness, the residue is dissolved in HCl (3 *N*), and the soln. is added to the column. The column is washed with HCl (7 *N*) (30 ml) and the washings are combined with the eluate and used for the determination of Ni, SO_4^{2-} and PO_4^{3-}.

K. SAITO

2176. **Spectrochemical analysis of electronic nickel alloys.** L. Vecsernyés (Res. Inst. for Telecommunication, Budapest). *Magyar Kém. Lapja*, 1958, **13** (7–8), 300–301.—A new method is described for the determination of Zn, Pb, Mg, Al, Cu, Mn, Fe, Cr and Co. The sample is dissolved in HCl, HNO_3 is added and the pptd. W is separated, ignited and determined gravimetrically. The filtrate is evaporated thrice to dryness and finally dissolved in *N* HCl to obtain a concn. of Ni of 40 g per litre for the spectrographic analysis. An alternating current interrupted-arc technique with a soln. dropping method is employed. The emission spectrum is compared with that of several spectrographically pure nickel soln. containing added amounts of the test metals in various concn. An improved method is described to obtain spectrographically pure Ni for a standard soln. An ISzP22 medium dispersion quartz spectrograph is used with a Zeiss 3 grade filter. Full details of the applied spectrographic and photographic techniques and reference-line wavelengths for the metals are given. The method may be used within the following concn. ranges (%)—Al (0·01 to 1·0), Mg (0·001 to 0·5), Mn (0·001 to 0·5), Fe (0·001 to 1·0), Cu (0·001 to 0·1), Cr (0·001 to 0·1), Co (0·01 to 2·0), Zn (0·01 to 1·0), and Pb (0·01 to 1·0). Results are accurate to within $\pm$ 5%.

G. SZABO

2177. **Paper chromatography in the separation of ions. II. Separation of precious metals.** A. K. Majumdar and M. M. Chakrabartty (Jadavpur Univ., Calcutta). *Anal. Chim. Acta*, 1958, **19** (2), 129–131.—Ascending paper chromatography is applied to Pd^{2+}, Pt^{4+}, Ir^{4+}, Rh^{3+}, Ru^{3+}, Os^{4+} and Au^{3+}. Eighteen different solvents are used, comprising various combinations of acetone or *tert.*-butyl alcohol with water and HCl or acetic acid, and the same mixtures containing also the complexing agents NH_4I, thiourea, bismuthiol I and II and 2-mercaptobenzothiazole. The chromatographic constants of the metals are recorded, and the values indicate that the separation of some mixtures containing up to five components is possible. H. N. S.

2178. **Spectrophotometric determination of rhodium with stannous bromide.** S. S. Berman and R. Ironside (Div. Appl. Chem., Nat. Res. Council, Ottawa, Canada). *Canad. J. Chem.*, 1958, **36** (8), 1151–1155.—The reaction between $SnCl_2$ and rhodium salts in the presence of HBr (*cf. Anal. Abstr.*, 1957, **4**, 1234) can be utilised for the rapid spectrophotometric determination of Rh if a chloride-free reagent is used and the deep-yellow complex is stabilised with a large excess of $HClO_4$. The reagent is a 20% (w/v) soln. of SnO_2 in 40% HBr. The Rh should be separated initially from Pt and associated noble metals, although an equiv. amount of Ir can be tolerated. *Procedure*—Dilute the sample soln. to $\simeq$ 5 ml with H_2O, add conc. $HClO_4$ (10 ml) plus $SnBr_2$ soln. (2 ml), and make the vol. up to 25 ml with H_2O. After 20 min. measure the extinction at 427 mμ (1-cm cell) against the reagent blank. Beer's law is valid from 0·8 to 1·6 p.p.m. of Rh, but high accuracy is still attainable between 0·4 and 4·0 p.p.m. With a slightly modified procedure, the method is applicable to samples that have been fumed with H_2SO_4. Factors that influence the intensity and stability of the coloured complex are discussed briefly. W. J. Baker

2179. **1-(2-Pyridylazo)-2-naphthol as a reagent for the determination of palladium.** A. I. Busev and L. V. Kiseleva (School of Anal. Chem., Univ., Moscow). *Vestn. Moskov. Univ.*, 1958, (4), 179–186.—The reagent 1-(2-pyridylazo)-2-naphthol (**I**) forms a green colour with $PdCl_2$ in dil. acid soln. (*e.g.*, 0·001 *M*) or an almost black voluminous ppt. of composition **I**.$PdCl_2$ in more concentrated soln. On heating, the colour forms even at pH 10. The compound is soluble in organic solvents at pH 2 to 5, $CHCl_3$ giving the most intense colour. The green soln. in $CHCl_3$ has absorption maxima at 620 and 675 mμ, with a mol. extinction coeff. of 16,000. The extracts obey Beer's law for 2 to 20 μg of Pd per ml. For the photometric determination of Pd, add 2 ml of a 0·1% soln. of **I** in methanol to 5 ml of soln. at pH 2·5, heat for 2 min. on a boiling-water bath, extract the complex with $CHCl_3$ (10, 5 and 5 ml), dilute the extracts with $CHCl_3$ to 25 ml and measure the extinction at 620 mμ. The content of Pd is found from a calibration curve. No interference is caused by the presence in the extract of 80 μg of Pt, 20 μg of Ir, 20 μg of Rh and 10 μg of Os per ml when determining 6 to 14 μg of Pd per ml. The pptn. of Pd from HCl soln. with **I** is possible in a wide range of acid concn. With *N* HCl only Pd is pptd.; at lower acidities (pH 1), the specificity is lost and Fe^{3+}, Bi^{3+} and Cu^{2+} begin to precipitate. First wash the ppt. of **I**.$PdCl_2$ with water to a colourless filtrate, and then with methanol. The air-dried ppt. is practically unchanged in wt. on heating to 115°. C. D. Kopkin

2180. **Separation of rhodium and iridium by multiple fractional extraction.** E. W. Berg and W. L. Senn, jun. (Louisiana State Univ., Baton Rouge, La., U.S.A.). *Anal. Chim. Acta*, 1958, **19** (2), 109–113.—A soln. of Rh and Ir in 6 *N* HCl saturated with NaCl is extracted with tributyl phosphate in nine stages, following the technique of Bush and Densen (*Brit. Abstr. C*, 1949, 110), whose theoretical treatment is also applied. The Rh is recovered in 99% yield from the raffinate and the Ir in 94% yield from the extractant, each metal being obtained free from the other. H. N. S.

2181. **Complex compounds of iridium and rhodium with thiourea and their application to the separation and determination of these metals.** N. K. Pshenitsŷn and I. V. Prokof'eva. *Zhur. Neorg. Khim.*, 1958, **3** (4), 996–1001; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,729.—It is established that Rh, Ir, Pt, Pd and Ru are quant. pptd. with thiourea (**I**). A gravimetric method is evolved for the determination of Rh and Ir with **I**, comprising the decomposition of the complexes of these metals with **I** by heating with conc. H_2SO_4. The error in determining 2 to 20 mg of Rh and Ir is $\gtrsim$ 3%. No interference to the determination of the platinum metals by this method is caused by the presence of Fe, Ni or Se in low concn. Copper, Pb and Sn are partially co-pptd., and Te is completely co-pptd. The method of pptg. the sulphides of the platinum metals by decomposing the complexes with **I** by warming with H_2SO_4 may be used to concentrate these metals. C. D. Kopkin

2182. **Methods for quantitative measurement of iridium content in platinum.** G. Airoldi and E. Germagnoli (CISE Lab., Milan). *Energia Nucleare, Milan*, 1957, **4**, 301–306 (in English).—The Ir content of a very pure sample of platinum (1·18 $\pm$ 0·34 $\times$ 10^{-3} atom %) has been determined by using two techniques of activation analysis. The reaction—

$$^{190}Pt \xrightarrow{n,\gamma} {}^{191}Pt \xrightarrow[29\ min.]{\beta} {}^{191}Au \xrightarrow[3{\cdot}5\ days]{\beta} {}^{191}Hg,$$

was used as an internal standard to calculate the Ir concn. from ^{192}Ir activity. The second method consisted in measuring the activity of ^{192}Ir after allowing the Pt activities to decay (49·4 days). An independently measured value of the neutron flux was used in this calculation. Activity measurements were made by using a NaI(Tl) crystal spectrometer and a 10-channel pulse analyser.

Chem. Abstr.

2183. **Analysis of fluorite containing large amounts of galena.** V. Skřivánek (Res. Inst. of Ores). *Chem. Listy*, 1958, **52** (9), 1827–1828.—A mixture of HCl, H_3BO_3 and $KClO_3$ has been suggested for the decomposition of the sample and EDTA for masking some elements (Pb, Fe, Al, Mn, Zn, Mg). *Procedure*—Heat the finely powdered sample (1 g) for 1 hr. with acetic acid (10%) (20 ml). Filter, wash with H_2O, and ignite the filter at $\gtrsim$ 700°. When necessary, determine the content of carbonate-bound Ca in the filtrate as oxalate. To the ignited residue add H_3BO_3 (0·5 g) and conc. HCl (30 ml) and heat for 30 min. till CaF_2 is decomposed. Add a small amount of $KClO_3$ and heat until all the galena is decomposed. Dilute with H_2O (40 ml), neutralise with aq. NH_3 and make acid with HCl. Set aside for 2 hr., filter, and wash the ppt. with hot

H_2O. Ignite the residue on the filter and weigh as SiO_2 and $BaSO_4$. To the filtrate add EDTA (disodium salt) (2 to 5 g), heat until dissolved and neutralise with aq. NH_3 to methyl red. Determine the Ca as oxalate. J. ZÝKA

2184. **Routine total analysis of cupola slag.** B. Bieber and Z. Večeřa (VUMT, Výzkum Slévárenský, Brno, Czechoslovakia). *Slévárenství*, 1957, **9**, 73–82.—A new method of total analysis of cupola slag in 100 to 120 min. has been proposed and examined. Silica is determined gravimetrically after evaporation with NH_4Cl; total Fe by the photometric method with KSCN; Al_2O_3 by the complexometric method with re-titration by Zn acetate, with Eriochrome black T (**I**); TiO_2 by the photometric method, with **I**; CaO by the complexometric method, with the mixed indicator of murexide and Naphthol green; the total of CaO and MgO by the complexometric method, with **I**; Na_2O and K_2O flame-photometrically; S volumetrically after the decomposition of the sample in a Mars furnace in a stream of oxygen; and P_2O_5 by the photometric method with molybdate and vanadate. The proposed method reduces the time necessary for carrying out the total analyses of the cupola slag in foundry laboratories and ensures better control of the fusion conditions in cupolas. The method can also be used for the analysis of silicates, having a similar composition to cupola slags, which decompose on treatment with acids, and for the analysis of blast-furnace and steel-works slags, etc.
CHEM. ABSTR.

2185. **Spectroscopic determination of iron, titanium, calcium and magnesium in clays and fireclays.** G. Dümecke and J. Wiegmann (Dtsch. Akad. Wiss., Berlin). *Silikat Technik*, 1957, **8**, 324–328.—The method recommended is based on mixing the sample (calcined at 960°) with a silver powder of high degree of purity in a ratio 1:5. This mixture is pressed in a special steel mould to rod-shaped electrodes for direct use in the high-voltage emission spectrometer. Three carefully analysed clays are used as reference standards for establishing the fundamental calibration curves for the lines Fe 2750·14, Ti 3361·21, Ca 3968·47, Ca 3158·87 and Mg 2790·79 *vs.* Ag 2721·71. These elements can be determined rapidly to within 5% in other clays and fireclays. For Mg, the use of a three-step filter (10, 50, 100% transmittance) is recommended; for Mg 2790·79, the 50% filter step is used, and for Ag 2743·90, the 10% filter step. CHEM. ABSTR.

2186. **Possibilities and limitations in the X-ray mineral analysis of bauxite.** H. Ginsberg and K. Wesers (Ver. Aluminium-Werke G. m. b. H., Bonn, Germany). *Z. Erzbergbau u. Metallhüttenw.*, 1957, **10**, 499–503.—A number of tests on various bauxite samples with an Iso-Debyeflex X-ray apparatus with a Berthold counting-tube goniometer leads to the conclusion that it is impossible by X-ray methods to determine the proportions of $Al(OH)_3$ minerals and kaolinite in bauxite. A qual. picture is possible. CHEM. ABSTR.

2187. **Determination of niobium and tantalum in titanium dioxide pigments.** L. G. Stonhill (Laporte Titanium Ltd., Luton, Beds., England). *Analyst*, 1958, **83**, 642–644.—When titanium dioxide is used as an opacifier in white enamel some minor constituents affect the colour of the product and Nb in particular causes an undesirable blue tinge. Methods were sought for the determination of Nb and Ta in titanium ores. With ilmenite a preliminary concentration of the earth oxides was achieved by fusion with potassium pyrosulphate, hot aq. leaching of the melt and recovery of any dissolved Ti, Nb or Ta by pptn. with aq. NH_3 after addition of NH_4Cl and EDTA. The modified method with EDTA and tannic acid of Das *et al.* (*Analyst*, 1956, **81**, 239) may also be used. The method chosen for separation of Nb and Ta from Ti and residual P and W was that of separation on a cellulose column (Mercer and Wells, *Ibid.*, 1954, **79**, 339). A pure concentrate of Nb and Ta having been obtained, the methods of Hunt and Wells (*Ibid.*, 1954, **79**, 345) and Marzys (*Ibid.*, 1954, **79**, 327; 1955, **80**, 194) were used, the latter being preferable for routine work. The Nb and Ta contents of some titanium ores are given, with indications of the method of separation used. A. O. JONES

See also Abstracts—**2002**, Use of pyridine deriv. in analysis. **2003**, Dimethylaminodiphenylantipyrinyl carbinol in inorganic analysis. **2004**, 7-Amino-1-methylphenoxaz-3-one as a reagent. **2005**, Phenylhydrazinethioformic acid as a reagent. **2187**, Determination of Nb and Ta in titanium dioxide. **2197**, Determination of Se in org. compounds. **2245**, Determination of metal content of paint driers. **2257**, Photometric determination of V. **2371**, Analysis for Zn, Cd and Cu in electroplating wastes. **2380**, Determination of H_3PO_4 in dicalcium phosphate. **2403**, Determination of radiochemical purity by electrophoresis. **2406**, Determination of Si in steel. **2428**, Apparatus for determination of F. **2452**, Apparatus for fluorination of U.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

2188. **Application of the method of radio-indicators to organic analysis.** P. Daudel. *Chim. Anal.*, 1958, **40** (9), 325–331.—Principles and applications of radiochemical methods are reviewed. *Activation*—This has been applied to DDT derivatives on a paper chromatogram, and to the determination of $> 0{\cdot}015$ μg of C by measuring the ^{13}N activity produced. *Radioactive reagents*—Acidic groups on cellulose can be made to react with ^{144}Ce acetate and the β-activity measured; amino acids are treated with radioactive CH_3I or with ^{64}Cu. Measurement of equiv. wt. is also possible. *Isotopic dilution*—This has been used to determine γ-hexachlorocyclohexane, and traces of ethers in the presence of esters. *Isotopic exchange*—Alkyl iodides may be determined in the presence of aryl iodides.
P. D. PARR-RICHARD

2189. **Micro-detection of hydrogen in organic compounds.** F. Feigl and E. Jungreis (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1958, (6), 812–813 (in English).—A far more sensitive test than hitherto available for the detection of H in organic compounds is based on the production of H_2S when they

are heated with sulphur. *Procedure*—Place a small portion of the solid or the evaporation residue of its soln. in a micro test-tube after mixing with a few centigrams of pure sulphur, and cover the mouth of the tube with a disc of Pb acetate paper. Heat at 220° to 250° in a glycerol bath. If organic matter containing H is present, a brown-black stain appears on the test paper within 2 min. The intensity of the colour depends on the quantity of H present. Hydrogen was detected in amounts of sample substance varying from 0·05 to 0·5 μg and no H_2S was yielded by 0·5-g quantities of several H-free compounds. D. F. PHILLIPS

2190. **Micro-determination of carbon and hydrogen.** N. F. Egorova and A. S. Zabrodina (School of Org. Chem., Univ., Moscow). *Vestn. Moskov. Univ.*, 1958, (4), 235–238.—The substance (3 to 9 mg) is ignited in a transparent quartz tube of diam. 19 to 20 mm with a rate of flow of O of 30 to 40 ml per min. An electric furnace of length 12 cm is placed near the end of the tube, a second movable furnace of length 6 cm is placed next to it. These furnaces first decompose the substance and then ignite the decomposition products at 850° to 900°. The ignition takes no longer than 2 to 4 min., after which a further 250 or 300 ml of O is passed at a rate of 50 to 60 ml per min. The whole procedure takes 7 to 10 min. The accuracy of the determination is ± 0·2%. If the organic substance contains halogen or S, metallic silver and platinum are placed in the ignition tube. C. D. KOPKIN

2191. **Simultaneous micro-determination of carbon, hydrogen and sulphur.** E. I. Margolis and N. F. Egorova (School of Org. Chem., Univ., Moscow). *Vestn. Moskov. Univ.*, 1958, (4), 209–213.—The SO_2 obtained on igniting organic S-containing compounds in a stream of O is absorbed with strontium silicate. To determine C, H and S, attach a weighed quartz tube containing strontium silicate to the ignition tube, heat at 600° for 5 to 7 min. while passing O at a rate of 35 to 50 ml per min., connect up the train for absorbing CO_2 (with ascarite) and H_2O (with anhydrone), pass O at 15 to 20 ml per min., introduce the sample (4 to 8 mg) with a 1·5-g platinum spiral and ignite. After the ignition, continue passing O at the same rate for 8 to 10 min., remove the furnace and pass O at 35 to 50 ml per min. for 12 to 15 min. Dismantle the train and after 10 min. weigh the absorption tubes. The error of the determination is ± 0·2 to 0·3% for all three elements. If S is not to be determined, the SO_2 may be absorbed on strontium silicate at the end of the ignition tube, with a rate of flow of O of 10 to 12 ml per min. The accuracy in determining C and H is ± 0·2%. The strontium silicate is ignited at 600° to 650° before use; its preparation is described. C. D. KOPKIN

2192. **Micro-determination of oxygen in organic substances.** F. Ehrenberger, S. Gorbach and W. Mann (Farbwerke Hoechst A.-G., Frankfurt am Main, Germany). *Mikrochim. Acta*, 1958, (6), 778–788.—Oxygen is converted into CO by carbon contact at 1120° to 1140° by the usual method, and after purification from interfering gases the CO is oxidised by means of iodine pentoxide. The resulting CO_2 is passed through a sinter into dil. $Ba(OH)_2$ soln. at about pH 11 and determined potentiometrically with automatic titration according to the method of Oelsen *et al.* (*Brit. Abstr. C*, 1952, 191) for the determination of C in steel. The method offers a saving in time over previous methods, is not less accurate and is simpler in operation. It has proved reliable even for the determination of traces of C as well as for samples containing much halogen and sulphur. Potentiometric indication of the end-point permits a better insight into the course of the analysis, gives an objective end-point and shows the method to be free from blank values. D. F. PHILLIPS

2193. **Determination of halogen in organic compounds by automatic coulometric titration.** O. E. Sundberg, H. C. Craig and J. S. Parsons (American Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1842–1846.—An automatic titrator is used for the determination of halides after fusion with Na_2O_2 in the Parr bomb. The halide is pptd. by generation of Ag^+ from a silver anode and the current required is measured by an integrating motor; the titration is automatically terminated by a titrator control unit. The coeff. of variation is ± 0·4%. G. P. COOK

2194. **Determination of chlorine and bromine by the high-temperature combustion method.** S. W. Nicksic and L. L. Farley (Calif. Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1802–1804.—The high-temp. combustion procedure was adapted to compounds containing Cl and Br. Sodium bisulphite soln. was used to absorb chlorine and bromine and to convert them quant. into the ionic form for subsequent titration with $AgNO_3$. Recoveries were generally >96% and the results compared well with the values obtained by other methods. G. P. COOK

2195. **Determination of chlorine and bromine in organic compounds using magnesium nitride.** A. P. Terent'ev, S. I. Obtemperanskaya and N. V. Ermolenko. *Nauch. Dokl. Vŷssh. Shkolŷ, Khim. i Khim. Tekhnol.*, 1958, (1), 83–85; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,359.—A simple, safe and rapid method proposed for the determination of Cl and Br in organic substances is based on the reductive decomposition of the sample with magnesium nitride (**I**) at 650° to 800° and subsequent Volhard determination of the halide ions in the magnesium salts formed. Decompose the sample (20 to 70 mg) in a refractory tube (22 cm × 1 cm) by heating so that the vapours pass slowly through the ignited zone of **I**. Heat the sample at red heat for 30 min. after charring and the cessation of gas evolution, cool, transfer the contents of the tube into 25 ml of water in a flask, acidify the resulting soln. with HNO_3, filter off the ppt. of carbon and determine halide ion in the filtrate. The method may also be used on the micro scale by using a shorter and narrower tube and a correspondingly smaller layer of **I**. The reaction takes 5 to 10 min. The error of the determination is < ± 0·3%. C. D. KOPKIN

2196. **Determination of bromine and chlorine in organic compounds by a modified Schöninger method.** K. Praeger and H. Fürst (Inst. für Org.-Tech. Chem., Tech. Hochschule, Dresden). *Chem. Tech., Berlin*, 1958, **10** (9), 537–538.—The combination of Schöninger's combustion analysis with the mercurimetric chloride titration according to Lapin makes it possible to determine bromine and chlorine in organic compounds even when the samples contain nitrogen or sulphur. The chloride or bromide, formed during the combustion, is titrated in weak acid soln. against 0·05 *N* $Hg(NO_3)_2$,

with diphenylcarbazide in ethanol as indicator. The modified method is quicker than the original one and independent of the size of the samples. Its accuracy is within ± 1·0 and ± 0·8% for Cl and Br, respectively. It is recommended for use in industry when quick analyses of organic chlorine or bromine compounds are required. L. M. RIEGELHAUPT

2197. **Micro-determination of selenium in organic compounds containing carbon, hydrogen, oxygen, nitrogen and selenium.** A. S. Zabrodina and M. R. Bagreeva (School of Org. Chem., Univ., Moscow). *Vestn. Moskov. Univ.*, 1958, (4), 187–192.—The ignition tube consists of a 50-cm tube of diam. 9 or 10 mm, narrowing at the exit-end to 3 mm; the narrow tubing is bent through a right angle and dips into 7 or 8 ml of water in a 10-ml cylinder. An electric furnace giving 800° to 900° is placed 6 or 7 cm from the constriction, and the sample (4 to 6 mg, 0·8 to 3 mg of Se) is placed 3 or 4 cm from the furnace. Ignite the sample with a burner in a stream of O flowing at a rate of 20 to 25 ml per min; white crystals of SeO_2 form on the walls of the tube beyond the furnace—this section of the tube is preferably cooled with wet cotton wool. After the ignition remove the furnace, clamp the tube at an angle and cool in the flow of O. Replace the oxygen intake with a Mariotte flask serving as an aspirator, open the tap and suck the water up to just beyond the layer of sublimed SeO_2, close the tap and remove the Mariotte flask to allow the soln. of H_2SeO_3 to drain into the cylinder, from which it is poured into the titration flask. Repeat the rinsing (× 2), the last time carefully heating the tube. Evaporate the soln. of H_2SeO_3 to 10 or 15 ml, cool, add 5 ml of $CHCl_3$, 1 ml of 20% KI soln. and 2 ml of 6 *N* H_2SO_4, close the flask and heat to not above 50° for 1 or 2 min. to convert the red amorphous Se (which adsorbs iodine) to the black modification. Cool, set aside in the dark for 10 min., dilute with water (35 to 40 ml) and titrate with 0·01 *N* $Na_2S_2O_3$. The error is ≯ ± 0·3%.
C. D. KOPKIN

2198. **Titrimetric determination of unsaturation by catalytic hydrogenation.** W. Seaman (American Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1840–1842.—Hydrogen gas is generated from standard aluminium lithium hydride, and introduced into a methanolic soln. of the sample with PtO catalyst in suspension. After the sample has been hydrogenated by shaking for a short time, the excess of H is caused to react with O to form H_2O, which is titrated with Karl Fischer reagent. The coefficient of variation ranged from 3 to 13%.
G. P. COOK

2199. **Organic quantitative analysis. XIX. Micro-determination of alkoxyl groups.** M. Večeřa and A. Spěvák (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (8), 1520–1525.—The method for the determination of alkoxyl groups (C_1–C_4) has been modified by the use of dry absorption (antimony potassium tartrate on kieselguhr) of interfering substances. Several difficulties connected with the use of absorption in liquids were thus avoided. Statistical evaluation of the results of the analysis showed that the accuracy of the new method is comparable with that of commonly used methods of elementary micro-analysis. The method has been tested by analysing vanillin, 4-ethoxydiphenyl, phenacetin, 4-propoxydiphenyl and *n*-butyl phenylcarbamate.
J. ZÝKA

2200. **Determination of the primary amino group in the presence of a secondary amino group.** A. Spiliadis, E. Bădic and D. Brețcanu. *Rev. Chim., Bucharest*, 1958, **9** (7–8), 471–473.—The authors have investigated (*i*) the effects of temp., excess of HNO_2, and concn. of acid during diazotisation; (*ii*) the optimum pH for coupling, the nature of the coupling component, its solubility at optimum pH and excess of coupling component; and (*iii*) the effect of the solubility of the excess of the coupling agent at various pH values. The method described consists in diazotisation of an aminodiphenylamine derivative, coupling with 2-naphthol and the determination of the excess of 2-naphthol by coupling with a *p*-nitrophenyldiazonium salt.
H. SHER

2201. **Micro-determination of several functional groups. I. Carboxylic anhydrides and lactones. II. Mercapto groups. III. Disulphides and dialkyl sulphides. IV. *iso*Cyanate and *iso*thiocyanate groups.** H. Roth (Landwirtschaftl. Versuchssta. Limburgerhof, Badische Anilin- & Soda-Fabrik A.-G., Ludwigshafen/Rhein, Germany). *Mikrochim. Acta*, 1958, (6), 766–777.—Detailed procedures for four simple methods are described. A method is given for distinguishing anhydrides and lactones of carboxylic acids from carboxylic acids and for their determination in the presence of such acids. A micro modification of the method of Menshutkin and Vasiliev (*J. Russ. Phys. Chem. Soc.*, 1889, **21**, 192) for the bromimetric determination of carboxylic acid anhydrides with 2:4-dichloroaniline is also given. Mercapto groups can be determined accurately in indifferent solvents by means of organic Cu^{II} salts and iodide. Disulphides and dialkyl sulphides can be determined by oxidation to sulphones with Br. *iso*Cyanate and *iso*thiocyanate groups are converted into alkylated ureas or thioureas by condensation with dibutylamine, the excess of which is measured by back-titration. The method is adapted from the macro-determination of Siefken (*Annalen*, 1949, **562**, 100).
D. F. PHILLIPS

2202. **Comments on the analysis of gas mixtures.** J. A. Barnard and H. W. D. Hughes (Univ. Coll., London). *Chem. & Ind.*, 1958, (34), 1109–1110.—Further modifications of the absorption methods of Stover *et al.* (*Anal. Chem.*, 1949, **21**, 1013), Saunders and Taylor (*J. Chem. Phys.*, 1941, **9**, 618) and Garrison and Burton (*J. Chem. Phys.*, 1942, **10**, 730) for the analysis of mixtures of carbon monoxide, oxygen and methane are listed. E. G. CUMMINS

2203. **Anomalous behaviour of *gem*-diethers in the mass spectrometer.** R. B. LeBlanc (Dow Chemical Co., Freeport, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1797–1799.—*gem*-Diethers give different mass spectra on a bare tungsten and a carbonised tungsten filament. The bare filament causes the partial decomposition of the *gem*-diether into a vinyl ether and an alcohol which may be due to (*i*) the catalytic action of the bare tungsten, or (*ii*) the higher operating temp. of the bare filament. For reliable analysis of these compounds it is recommended that a carbonised filament be used. Ten nights of conditioning with styrene were required to attain a stable condition towards the *gem*-diethers.
G. P. COOK

2204. **New reagent for detection of sucrose.** J. Hadi. *Cukoripar*, 1958, **11**, 225–226, and err. p. 280a.—Camphor in H_2SO_4 gives a bright-red colour

with sucrose. The reaction can be used for photometric quant. analysis. A 1% soln. of camphor in conc. H_2SO_4 (time of dissolution $\simeq$ 10 min.) is pale yellow; 1 to 1·5 ml of soln. is added to 1 ml of the soln. to be tested (previously cooled). The max. colour strength develops in 5 min. The test is sensitive to 5 p.p.m. of sucrose, and can be used quant. up to 1 mg per ml. For many purposes, visual estimation is suitable. The reaction may also be carried out as a ring test. The disadvantage of the pink colour of 1-naphthol soln. is avoided by the use of camphor. SUGAR IND. ABSTR.

2205. **Determination of small quantities of sugars in aqueous solutions. (Application to re-utilised waters in sugar manufacture.)** A. Lemaitre. *Sucr. Franç.*, 1958, **99**, 250–251.—The sensitivities and merits of different colour reactions for sucrose in alkaline or acid medium are briefly surveyed. The reaction with phenol (80% soln.) in acid soln. is preferred. Mix 2 ml of sucrose soln. with 0·05 ml of phenol in a test-tube, add 5 ml of conc. H_2SO_4 rapidly (20 sec.) and mix. Set aside for 10 min., cool to 25° (in 10 min.) and measure the colour intensity with a photocolorimeter at 490 mμ. The sensitivity is at least 5 p.p.m. The sucrose concn. is directly proportional to the absorption.
SUGAR IND. ABSTR.

2206. **Determination of small amounts of sucrose with the anthrone reagent.** L. Pausz and J. Hadi. *Cukoripar*, 1958, **11**, 259–261.—Laboratory tests have been made of the quant. determination of small amounts of sucrose in condensate waters with anthrone for use in an automatic control apparatus (*cf. Sugar Ind. Abstr.*, 1956, **483**). The preparation of the reagent is described; the colour was measured by means of a Lange-Roth photometer with yellow filter. The time of waiting for max. development of the colour was tested at 1-min. intervals; 15 min. was usual, but shorter times were required for low sugar concn. It is essential for the reagent to be freshly prepared each day.
SUGAR IND. ABSTR.

2207. **Separation of sucrose, glucose, fructose and sorbitol by combined chromatography and electrophoresis.** S. Gerlaxhe and J. Casimir. *Bull. Inst. Agronom. Gembloux*, 1957, **25**, 265–268.—Sucrose, fructose and glucose with sorbitol were separated by chromatography on a band of paper with benzene, butanol, pyridine and water (1:5:3:3) as solvent. The band was placed on a paper strip and glucose and sorbitol were separated by electrophoresis, by using borate buffer, pH 7 or 7·5.
NUTR. ABSTR. REV.

2208. **Comparative studies on six methods of determining fructose in the presence of glucose.** Y. Matsuo and A. Nanba. *J. Fermentation Technol.*, 1958, **32**, 342–347.—Three titration methods (Plank's method, an indirect method and Mathew's method) and three colorimetric determinations (diphenylamine, cysteine - carbazole and resorcinol - thiourea) for the determination of fructose in the presence of glucose were examined and compared. Of the three titration methods, the indirect method is the most accurate—glucose is determined by hypoiodite titration (optimum concn. 250 mg per 100 ml), total sugar is determined by the Bertrand method (optimum concn. 250 mg of sugar per 100 ml), and fructose is given by the difference between the total sugar and the glucose determinations. Of the three colorimetric methods, the cysteine - carbazole method (*cf. Sugar Ind. Abstr.*, 1951, 749) shows the least influence by the glucose on the fructose determination. The ratio of the absorption coeff. of fructose and glucose was 280:1. Some figures are given of fructose concn. in orange and persimmon juices; results by the three colorimetric methods were higher than by the indirect method.
SUGAR IND. ABSTR.

2209. **Direct estimation of xylose in hemicelluloses.** E. Bennett (Mass. Agric. Exp. Sta., Amherst, U.S.A.). *J. Agric. Food Chem.*, 1958, **6** (8), 618–619.—In developing a method for determining hemicelluloses in forage crops by means of the major component, xylose, the absorbances of glucose, galactose, arabinose, xylose, and glucuronic and galacturonic acids were measured after treatment with 79% H_2SO_4. It was found that subtracting the absorbance at 275 mμ from that at 315 mμ minimised the effects of the other sugars on the absorbance of xylose. Values obtained by this method for hemicelluloses in maize cobs and rye straw were 94% of those obtained with phloroglucinol, and recovery of xylose added to impure dispersions of hemicelluloses from clover and grass averaged 96%. M. D. ANDERSON

2210. **Determination of sorbitol in the presence of carbohydrates.** J. W. White, jun. (Eastern Regional Res. Lab., Eastern Utilization Res. and Development Div., Agric. Res. Service, U.S. Dept. of Agric., Philadelphia, Pa.). *Analyst*, 1958, **83**, 649.—Boiling the sample soln. with dil. Na_2CO_3 soln. has been recommended for the destruction of interfering sugars in the determination of sorbitol (Adcock, *Analyst*, 1957, **82**, 427), and in this procedure knowledge of the identity of the carbohydrates present is not necessary. A study of this procedure showed that all sugars are not removed by the treatment. Reducing sugars are quant. destroyed, but non-reducing sugars are not, and subsequently interfere in the determination of sorbitol with periodate. The identity of the carbohydrates present in a soln. to be analysed for sorbitol by Adcock's procedure must thus be known, especially when they are non-reducing sugars. Interference by such sugars can be avoided by the inclusion of a suitable hydrolysis step before the treatment with alkali. A. O. JONES

2211. **Determination of free formaldehyde in reaction products of thiourea with formaldehyde by means of the oxime titration method.** K. Dušek (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (9), 489–493.—The reaction of formaldehyde (**I**) with hydroxylamine hydrochloride has been used for the determination of free **I** in mixtures containing products of the reaction of **I** with thiourea. The determination is based on the titration of the HCl set free with a differential photometric indication of the end-point. The oximation reaction is carried out at a pH near neutrality so that a practically complete conversion of **I** into oxime takes place and the possibility of hydrolysis of hydroxymethyl derivatives of thiourea during the determination is avoided. Results are accurate to within ± 0·25%.
J. ZÝKA

2212. **Differentiation of organic acids in spot-test analysis.** F. Feigl and C. Stark-Mayer (Lab. da Produção Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Talanta*, 1958, **1** (3), 252–255.—When an

alkali or ammonium halide is heated at 160° with certain organic acids, HCl (HBr, HI) is released and can be detected with universal indicator paper. Aliphatic and aromatic polycarboxylic acids, arylalkyl carboxylic acids or aromatic monocarboxylic acids give positive results, also *o*-nitrophenol (but not its isomers) and picric acid. Aliphatic monocarboxylic, hydroxamic and sulphonic acids do not react. To a small sample in a micro tube add an excess of NaCl. Cover the mouth of the tube with moist indicator paper and heat at 160° in a glycerol bath; observe the colour of the paper after 2 to 5 min. The limits of detection are approx. 10 to 100 μg. For alkali or alkaline-earth salts of the acids, add NaCl to a sample and excess of dil. HCl; dry, heat at 120° for 10 min. then complete the test. Volatile monocarboxylic acids interfere; confirm the release of HCl by testing with $Ag_4Fe(CN)_6$ - $FeSO_4$ paper.

P. D. PARR-RICHARD

2213. **Separation and determination of organic acids by column chromatography.** A. Miss and G. Petrescu. *Rev. Chim., Bucharest*, 1958, **9** (7–8), 467–471.—Two simplified methods for the preparation of silica gel are given, together with a specification of granular content to permit the use of a column without pressure but without affecting its efficiency. For ordinary non-continuous work, a column of adsorbent 10 cm long in a tube 20 cm long × 1 cm wide, surmounted by a pear-shaped reservoir, is recommended. The tap at the bottom of the column is specially cut to permit fine regulation of the flow. For continuous work, a distillation flask containing $CHCl_3$, fitted with a separating funnel containing butanol, is connected to the top of the column. The tap of the funnel is set to give the increasing concn. of butanol required, while a magnetic stirrer homogenises the mixture, which overflows from the distillation arm into the top of the column. Should the polarity of the mixture increase too rapidly, then a corresponding mixture of butanol and $CHCl_3$ can be placed in the funnel. Details are also given of a method of following the course of fractionation of the acids with the use of thymol blue as indicator. H. SHER

2214. **Relation between structure and R_F value of aliphatic dicarboxylic acids.** V. Šanda, Ž. Procházka and H. Le Moal (Chem. Inst., Acad. Sci., Prague). *Chem. Listy*, 1958, **52** (8), 1546–1552.—The chromatographic behaviour of 39 dicarboxylic acids and of 9 monomethyl esters has been studied in the presence of some keto and hydroxy acids in two systems (butyl acetate saturated with H_2O, and CCl_4 containing 2% of acetic acid). The isomers of various types of compound, mainly *cis*- and *trans*-isomers, can be distinguished with the procedure described. The relation between structure and R_F values of the compounds studied is discussed. A freshly prepared 1% soln. of the acids in methanol (50 μg of the sample) was placed on Whatman paper No. 4 and after equilibrium between the paper (impregnated with 1% H_2SO_4) and the atmosphere had been reached (about 12 hr.) the chromatographic separation was carried out. A soln. of bromocresol green buffered with H_3BO_3 and $Na_2B_4O_7$ was used for the detection (yellow spot of the separated acids on a blue - green background). For the detection of glyoxylic acid the chromatogram must be moistened with a 1% soln. of phenylhydrazine hydrochloride and then with a 5% soln. of $K_3Fe(CN)_6$ diluted with HCl (1:1); a violet - red colour appears. J. ZÝKA

2215. **Complexometry in organic analysis. VI. A new method for the determination of organic bases.** B. Buděšínský and J. Kŏrbl (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (8), 1513–1519.—A new semi-micro method for the determination of tertiary amines, quaternary ammonium bases, their salts and analogous sulphonium derivatives is based on the pptn. reaction of acid soln. of these compounds with a soln. of the complex of Bi - EDTA (disodium salt) containing KI and on the titration of the liberated EDTA with a soln. of a thorium salt, at pH 2 to 3, with methyl thymol blue as indicator. *Procedure*—Dissolve the sample in 1·5 *N* HCl (5 ml) in a 10-ml centrifuge tube, add 5 ml of reagent soln. [dissolve 10·6 g of EDTA (disodium salt) with 19 g of KI and 12 g of $BiCl_3$ or $Bi(NO_3)_3$ in 700 ml of twice-distilled H_2O; to the orange soln. add, after shaking for 5 min., a soln. of 2 g of NaOH in 20 ml of H_2O and 4 g of $NaHSO_3$; the pH must not exceed 4 to 5; adjust the vol. to 1 litre with H_2O, shake for 10 min. and filter], mix and after 5 min. separate the ppt. by centrifuging (5 min.; 2000 rev. per min.) To 7 ml of the clear supernatant liquid add Na acetate soln. (20%) (4 ml) and dilute with twice-distilled H_2O (20 ml). Titrate with 0·01 *M* $Th(NO_3)_4$ till the indicator colour changes from yellow to blue. Good results were obtained with a variety of compounds. J. ZÝKA

2216. **Rapid method for determination of urea in nitrogen solutions.** J. A. Smith, D. G. Dock and R. W. Rich (Sohio Chem. Co., Lima, Ohio). *J. Agric. Food Chem.*, 1958, **6** (8), 587–588.—Urea in aq. soln. containing also NH_4NO_3 and NH_3 is determined rapidly and reliably, within 1%, by neutralising to methyl purple, incubating for 20 min. at 40° with 0·8 g of urease per 1 g of urea, and titrating with standard acid to the methyl purple end-point. M. D. ANDERSON

2217. **Application of anhydrous alkalimetry and chelatometry to the determination of the disodium calcium chelate of ethylenediaminetetra-acetic acid.** C. Hennart and E. Merlin. *Chim. Anal.*, 1958, **40** (9), 345–347.—EDTA (calcium disodium salt) may be determined by pptn. of Ca as oxalate after removal of organic matter. It is more satisfactory to determine both Ca and Na as follows. *Procedure for Ca*—Weigh 0·15 g into a nickel dish and ignite at dull red heat. Cool and dissolve the residue in 30 ml of *N* HCl. Boil to expel CO_2, cool to 60° and add 10 ml of Mg reagent and a little Eriochrome black T. Titrate with 0·02 *N* EDTA (disodium salt) at 50° to 60°. The Mg reagent contains EDTA (magnesium disodium salt) (4 g), NH_4Cl (11 g), NaCN (0·1 g) and conc. aq. NH_3 (70 ml) in 200 ml of boiled water. *For Ca plus Na*—Ignite 0·1 g as before, dissolve in 25 ml of $HClO_4$ - propionic anhydride reagent, rinse the dish with anhyd. propionic acid and add a little malachite green. Titrate with pyridine - propionic acid reagent to a yellow - green end-point. The $HClO_4$ - propionic anhydride reagent contains 95% propionic anhydride (35 g) and $HClO_4$ (*d* 1·69) (10 ml) in 1 litre of anhyd. propionic acid. Allow to stand for 24 hr. and standardise. The pyridine - propionic acid reagent contains 8 ml of pyridine in 1 litre of anhyd. propionic acid. It is standardised with the previous reagent.

P. D. PARR-RICHARD

2218. **The determination of Desmodur H (hexamethylene diisocyanate) in air.** S. von Eicken (Toxikolog. Lab., Farbenfabriken Bayer A.-G.,

Wuppertal-Elberfeld, Germany). *Mikrochim. Acta*, 1958, (6), 731–735.—The material is absorbed in a mixture (1:1) of dimethyl sulphoxide and 0·1 *N* HCl and the hexamethylenediamine obtained by saponification is treated with 1-fluoro-2:4-dinitrobenzene. The resulting condensation product is extracted with tetrachlorethane and measured photometrically at 366 mμ. The limit of detection is 0·002 p.p.m.

D. F. PHILLIPS

2219. **Quantitative measurement of ββ′-dichloroethyl sulphide (Yperite) and of β-chlorovinyldichloroarsine (Lewisite) by the potentiometric method.** P. Malatesta and A. Lorenzini (Ist. Chim. Farm., Univ., Rome). *Ric. Sci.*, 1958, **28** (9), 1874–1879.—A potentiometric determination of Yperite and Lewisite, using 0·02 to 0·05 *N* $KBrO_3$ and HCl, is described. With Yperite a back-titration can also be used. Organic chlorine atoms of ββ′-dichloroethyl sulphide are ionised by a short heating with triethylamine.

C. A. FINCH

2220. **Determination of dithiocarbamic acid derivatives in the presence of copper salts.** L. Carloni (Univ. of Pisa, Italy). *Ric. Sci.*, 1958, **28** (8), 1639–1643.—The original method of Clarke *et al.*, for the determination of dithiocarbamic acid derivatives in commercial anticryptogams, as modified by Fontana and Martelli (*Anal. Abstr.*, 1955, **2**, 3240), is re-examined. Determinations by the various procedures show that the high results obtained are due to the formation of HCN. When this is removed by the use of a silver nitrate absorber in the original Clarke apparatus, consistent results are obtained. The presence of larger amounts of copper salts causes results below theoretical.

C. A. FINCH

2221. **Titrations with sodium nitrite in organic analysis.** M. Matrka (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chemie, Prague*, 1958, **10** (8), 635–646.—A survey is presented of volumetric methods with visual, potentiometric, amperometric and dead-stop indication, in which $NaNO_2$ soln. is used as titrating agent. The titration of primary aromatic amines, diazotisation titration of secondary aromatic amines, tertiary aliphatic and aromatic amines, nitrosation of aromatic hydroxy compounds, and titration of derivatives of hydrazine and of arylsulphinic acids are described.

J. ZÝKA

2222. **Substitutive halogenation of aromatic compounds in aqueous solution by interhaloids. II. Preparation and investigation of a standard solution of bromine chloride.** E. Schulek and K. Burger (Inst. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Talanta*, 1958, **1** (3), 219–223.—In HCl, BrO_3^- react quant. with Br^- to give BrCl; a 0·1 *N* soln. in HCl is fairly stable for three months. If excess of BrO_3^- is present, Cl is formed. With 0·5 g of KCN and 20 ml of 2 *N* NaOH, BrCl gives CNBr, which hydrolyses to Br^- and CNO^-. On acidification, CNO^- give NH_4^+ and CO_2, and residual BrO_3^- is determined iodimetrically. A method is also given for the determination of Cl. *Reagent*—Dissolve 2·7835 g of $KBrO_3$ and 3·9670 g of KBr in 500 ml of H_2O, add 365 ml of 20% HCl and when the soln. is yellow make up to 1 litre with H_2O. *Standardisation*—(*i*) By iodimetry: add 10 ml of BrCl soln. to 0·5 g of KI in 30 ml of H_2O; titrate the iodine with $Na_2S_2O_3$ soln. (*ii*) With hydrazine: dissolve 0·3 g of hydrazine sulphate in 100 ml of H_2O, dilute 10 ml of this to ≯ 50 ml with H_2O, add 2 to 10 ml of 20% HCl or 10 to 20 ml of 2 *N* H_2SO_4 and titrate with 0·1 *N* BrCl, with *p*-ethoxychrysoidine as indicator.

III. Determination of aromatic compounds by bromination with bromine chloride. E. Schulek and K. Burger. *Ibid.*, 1958, **1** (3), 224–237.—Bromine chloride reacts with organic aromatic compounds solely as a brominating agent (*cf. Anal. Abstr.*, 1959, **6**, 611) and its use greatly increases the rate of bromination. This reaction was used for the determination of phenols. *Procedure*—Prepare a 0·1 *N* aq. soln. of the phenol (adding NaOH if necessary). Dilute a 5 to 10-ml aliquot with H_2O to 80 to 100 ml in a bromination flask. Add some $Br^- - BrO_3^-$ reagent and place 10 ml of 20% HCl in the wide part of the neck of the flask. Release the stopper to run in the acid and after bromination (1 to 3 min.) add KI. After 3 to 5 min. titrate the iodine with 0·1 *N* $Na_2S_2O_3$. Owing to the short bromination time, salicylic acid can be determined in the presence of acetylsalicylic acid. To prepare the reagent, dissolve 2·7835 g of $KBrO_3$ and 3·9670 g of KBr in H_2O and dilute to 1 litre.

P. D. PARR-RICHARD

2223. **Quantitative determination of methylene*cyclo*hexane and the isomeric methyl*cyclo*hexenes in their mixtures by infra-red spectroscopy.** S. Pinchas, J. Shabtai and E. Gil-Av (Weizmann Inst. Sci., Rehovoth, Israel). *Anal. Chem.*, 1958, **30** (11), 1863–1865.—Methylene*cyclo*hexane and the three isomeric methyl*cyclo*hexenes are quant. determined in CS_2 soln. at 700, 889, 918 and 1045 cm^{-1}. Results for synthetic mixtures agreed within 2% of the known compositions.

G. P. COOK

2224. **Identification of carcinogenic hydrocarbons.** F. Lickint and M. Büchner (I Med. Klin., Stadtkrankenhaus. Dresden-Friedrichstadt, Dresden, Germany). *Naturwissenschaften*, 1958, **45** (24), 625.—Polarographic analysis as an adjunct to chromatographic separation yielded satisfactory results. The requirements for the polarographic analysis are very stringent. Tetraethylammonium iodide or tetrabutylammonium iodide (0·05 *M*) is used as the electrolyte and must be recrystallised three times from 50% ethanol. As buffer soln. is used 0·01 *M* tetra-ethyl- or -butyl-ammonium hydroxide, reinforced with 0·01 *M* barbitone. The solvent is 90% ethanol. Continuous and vigorous bubbling with H is necessary to remove all air from the soln. Calibration curves with pure hydrocarbons must be prepared.

E. KAWERAU

2225. **Gas-liquid chromatographic resolution of *m*- and *p*-xylene: tetrahalophthalate liquid phases.** S. H. Langer, C. Zahn and G. Pantazoplos (Central Exp. Sta., Bureau of Mines, Pittsburgh, Pa., U.S.A.). *Chem. & Ind.*, 1958, (35), 1145–1147.—The use of methyl propyl and di-*n*-propyl tetrachlorophthalate and di-*n*-propyl tetrabromophthalate for this separation is illustrated with graphical data from results obtained with two columns. A toluene internal standard was used to obtain results for a commercial mixture of 'xylenes,' comprising toluene, 0·7; ethylbenzene, 4·0; *m*-xylene, 61·1; *p*-xylene, 22·7; *o*-xylene, 9·6; unidentified, 1·9%, which were verified with a synthetic mixture. The theoretical aspects are discussed.

E. G. CUMMINS

2226. **The diffusion coefficients of phenol in water.** E. Erdös and J. Nývlt (Inst. of Chem. Technol., Prague). *Coll. Czech. Chem. Commun.*, 1958, **23**

(4), 579–586.—A sensitive method for the determination of phenol in water is described. *Procedure*—Take a neutralised sample containing $\simeq$ 2 mg of phenol, dilute to 150 to 200 ml and add 0·1 *N* $KMnO_4$ (9 ml). Heat on a boiling-water bath for 30 to 60 min. and then acidify with H_3PO_4 (1:5) (10 ml). Add 0·05 *N* oxalic acid (20 ml) and back-titrate with 0·05 *N* $KMnO_4$. Carry out a blank determination. If a microburette is employed, the precision can be expected to be about 0·5%.

G. S. ROBERTS

2227. **The detection of phenols on paper chromatograms.** E. Hofmann and G. Hoffmann (Hauptversuchsanst. f. Landwirtsch. Weihenstephan, Germany). *Naturwissenschaften*, 1958, **45** (14), 337–338.—The dried chromatograms are sprayed with a freshly prepared 0·3% methanolic soln. of 2:6-dibromo-*p*-benzoquinonechlorimine. Drying in hot air causes some phenols to appear immediately; others do not appear until the paper receives a second spraying with 0·1% aq. $NaHCO_3$ soln. As little as 1 μg of most phenols can be detected. Strongly reacting are quinol (bluish-violet - grey), resorcinol (deep violet), catechol (grey - brown), phloroglucinol (grey - brown), pyrogallol (brown), gallic acid (grey), 1-naphthol (rose), 2-naphthol (red - violet), *o*- and *m*-cresol (blue), *o*-xylenol (light brown), *m*-xylenol (blue - violet), arbutin (blue), guaiacol (red - brown) and thymol (rose). Weakly reacting phenols are phenol (light blue) and *p*-cresol (yellow - brown); a very poorly reacting phenol is tyrosine. No reaction is given by *p*-hydroxybenzaldehyde.

E. KAWERAU

2228. **A new reagent for the detection of phenols on paper chromatograms.** F. Klinkhammer (Biochem. Lab., Chem. Pharmaz. Fabrik Schaper & Brümmer, Salzgitter-Ringelheim, Germany). *Naturwissenschaften*, 1958, **45** (23), 571.—The dried chromatograms are sprayed with an aqueous saturated soln. of ammonium vanadate. This reagent produces pale-yellow or brown spots, partly masked by the yellow colour of the reagent. While still wet the chromatograms are sprayed with an ethanolic soln. of *p*-anisidine rendered acid with H_3PO_4 (0·5 g of *p*-anisidine dissolved in 2 ml of H_3PO_4 and diluted to 100 ml with abs. ethanol). The phenols now appear as orange - yellow spots on a red background. The red anisidine vanadate complex of the background fades on drying but the colour of the phenol spots appears to be permanent. The following colours are given: quercetin (yellow), quercitrin (brown), caffeic acid (red), chlorogenic acid (pink), ferulic acid (grey - green), (+)-catechin (grey - brown) and phloroglucinol (bluish green). As little as 10 to 15 μg of the phenol can be detected by this reaction.

E. KAWERAU

2229. **Titration of weak acids in non-aqueous solvents. Conductimetric studies.** D. B. Bruss and G. A. Harlow (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1836–1839.—The titration of phenols has been studied with both a.c. and d.c. methods, and solvents with intermediate and low dielectric constants have been investigated as titration media. Phenols that are not sterically hindered exhibit conductimetric mid-point max., which indicate association of exceptional strength in benzene, xylene, toluene, carbon tetrachloride, pyridine, acetone and *iso*butyl methyl ketone.

K. A. PROCTOR

2230. **Titration of weak acids in non-aqueous solvents. Potentiometric studies in inert solvents.** G. A. Harlow and D. B. Bruss (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1833–1836.—The potentiometric titration of phenols and carboxylic acids is carried out with a non-aqueous soln. of a quaternary ammonium hydroxide as titrant, a pair of glass - calomel electrodes and a vibrating-reed electrometer. The titration curves obtained are normal when dilute titrant ($\gtrsim$ *N*) is used.

K. A. PROCTOR

2231. **Analysis of phenols and hydrocarbons by means of gas - liquid chromatography.** L. Sokl (Phys. Lab., Stalinovy Závody, Záluží, Czechoslovakia). *Chem. Listy*, 1958, **52** (9), 1726–1734.—A new glass apparatus for gas - liquid chromatography with conductivity indication is described. The value of the apparatus has been tested by separation of mixtures of hydrocarbons and ketones. The separation of phenols with the use of sulphones as solid phase has also been worked out. The influence of sulphone concn. in a mixed solid phase (methylsilicone oil - 1:2-dinaphthyl sulphone) on the separation of *o*-cresol from other cresols has been studied and it has been found that the presence of 5 to 20% of sulphone in the solid phase is sufficient for the quant. separation of *o*-cresol. The described apparatus is suitable also for determinations at higher temp. (300°).

J. ZÝKA

2232. **Detection and determination of aromatic polynitro compounds with ethylenediamine.** P. Engelbertz and E. Babel. *Zentr. Arbeitsmed. u. Arbeitsschutz*, 1957, **7**, 171–173.—The following colours were observed (the colours after addition of ethanol and the minimum concn. for the reaction are given in parentheses): adducts of ethylenediamine and *m*-dinitrobenzene, violet (colourless, 2×10^{-7}); *o*-dinitrobenzene, yellow (yellow, 4×10^{-6}); 2:4-dinitrotoluene, indigo (colourless, 6×10^{-6}); 2:3-dinitrotoluene, yellow (yellow, 4×10^{-6}); 3:4-dinitrotoluene, yellow (yellow, 5×10^{-6}); 2:5-dinitrotoluene, violet (colourless, 1×10^{-7}); 2:6-dinitrotoluene, rose (colourless, 2×10^{-5}); 3:5-dinitroanisole, indigo (colourless, 6×10^{-6}). A soln. of the nitro compound in water (30 ml) (10^{-5} to 10^{-6}), urine or serum was mechanically extracted with ligroin (boiling-range 80° to 120°), 30 ml of 70% ethylenediamine soln. was added, the mixture stirred for 20 min., centrifuged, and the extinction of the colour determined photometrically and compared with that of standard soln. Since the colour of the adducts is sensitive to light and heat the reactions were effected in brown glass and at 0°. For quant. separations of a mixture of *m*- and *o*- or *p*-dinitro compounds the colour of the adducts was determined before and after addition of ethanol and the values compared with standards.

CHEM. ABSTR.

2233. **Identification of organic compounds. XXVII. Use of Friedel - Crafts acylation in the identification of alkyl aryl sulphides.** J. Gasparič, M. Večeřa and M. Jureček (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (9), 1720–1725.—A new method for the identification of aromatic and aliphatic sulphides is based on their acylation with acetyl chloride in $AlCl_3$ according to Friedel - Crafts. The alkyl mercaptoacetophenones formed are converted into 2:4-dinitrophenylhydrazones, which can be distinguished by m.p. or by X-ray diffraction patterns.

J. ZÝKA

2234. **Detection limits of flavones with tetraphenyl diborate and long-chain quaternary ammonium compounds by means of Feigl spot reactions.** R. Neu (Firma Dr. Willmar Schwabe G.m.b.H., Karlsruhe, Germany). *Mikrochim. Acta*, 1958, (6), 715–725.—*Procedure*—Dissolve the flavone in methanol and by means of a micro-pipette apply to a S. & S. 2043a filter-paper successive aliquots of a 0·1% soln. containing from 10 to 1 μg of flavone. Repeat with aliquots from a 0·01% soln. containing from 0·5 to 0·1 μg of flavone. Examine the spots in daylight and u.v. light. The detection limits of 20 hydroxy derivatives of phenylbenzo-γ-pyrones and their glucosides were determined on the basis of the colour stains produced when examined in this way, together with the change in colour and detection limits by means of tetraphenyl diborate and by means of tetraphenyl diborate and long-chain quaternary ammonium compounds. Characteristic colour reactions are exhibited by flavone derivatives, which show that the colours obtained are dependent on the position and number of the hydroxyl groups. Thus indications of the structural constitution are yielded. The use of tetraphenyl diborate permits lower limits of detection than can be obtained by paper chromatography.

D. F. PHILLIPS

2235. **The detection of hydroxyphenylbenzo-γ-pyrones with aryl diborate in the presence of electron donators.** R. Neu (Firma Dr. Willmar Schwabe G.m.b.H., Karlsruhe, Germany). *Naturwissenschaften*, 1958, **45** (13), 311.—Flavones react with tetraphenyl diborate dissolved in dimethyl sulphoxide to yield compounds having very intense fluorescence. The differences in the reaction for different hydroxyphenylbenzo-γ-pyrones is so marked that inferences as to their structure may be drawn from close observation of the reaction. An orange - red fluorescence is given by quercetin and by rhamnetin and its three glucosides, though *iso*-rhamnetin does not react. Luteolin has a yellow - orange fluorescence. Absence of the 3′-hydroxy group is shown by the fluorescence turning to a yellow - green. Among the 40 flavones (and glucosides) examined, 5 different fluorescent colours could be observed which depend on the position and number of the hydroxyl groups. E. KAWERAU

2236. **A test for quinic acid.** R. Neu (Firma Dr. Willmar Schwabe G.m.b.H., Karlsruhe-Durlach, Germany). *Naturwissenschaften*, 1958, **45** (12), 286.—Quinic acid when separated on a paper chromatogram reacts with a flavonol, preferably the 3:5:7:2′:4′-pentahydroxy derivative of phenylbenzo-γ-pyrone, which yields a reddish-violet or white spot that shows an intense red or blue - violet fluorescence in u.v. light. The γ-lactones of other polyhydroxycarboxylic acids give similar reactions with the reagents, but can be distinguished by their different R_F values. A 0·25% methanolic soln. of the flavonol is recommended as a spray reagent.

E. KAWERAU

2237. **Aromatic hydrocarbons in the 170° to 180°C fraction of petroleum.** B. J. Mair, S. P. Davidson, N. C. Krouskop and F. D. Rossini (Carnegie Inst. Technol., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1814–1817.—The aromatic portion of the representative petroleum under investigation by API Research Project 6, boiling normally in the range 170° to 180°, was found to consist substantially of seven hydrocarbons. The relative amounts are—1:2:3-trimethylbenzene, 54·5%; 1-methyl-3-*iso*propylbenzene, 22·6%; 1-methyl-4-*iso*propylbenzene, 12·1%; *sec.*-butylbenzene, 5·0%; 1-methyl-2-*iso*propylbenzene, 2·5%; *iso*butylbenzene, 2·4%; and indane, 0·9%. These compounds constitute 0·35% of the original petroleum. The compounds were isolated and concentrated by distillation and adsorption techniques and identified by physical and i.r. examination. G. P. COOK

2238. **Physicochemical characteristics of essential oils, essential oil constituents and their derivatives.** L. Levi (F. & D. Labs, Dept. Nat. Health and Welfare, Ottawa, Canada). *Perfum. Essent. Oil Rec.*, 1958, **49** (9), 512–528.—Data and graphs are given for i.r. absorption spectra, near i.r. absorption spectra, u.v. absorption spectra, Raman spectra, nuclear magnetic resonance spectra and X-ray diffraction patterns for *trans-iso*eugenyl acetate and *trans*-benzyl *iso*eugenyl ether. N. E.

2239. **The detection of low-molecular-weight fatty acid esters in essential oils.** R. Pohloudek-Fabini and K. Luthardt (Pharmaz.-chem. Inst., Ernst-Moritz-Arndt-Univ., Greifswald, Germany). *Naturwissenschaften*, 1958, **45** (13), 314.—The method is an adaptation of the reaction described by Fink and Fink (*Proc. Soc. Exp. Biol. Med.*, 1949, **70**, 654). A drop of the essential oil is dissolved in 10 ml of ether and 1·5 ml of 5% hydroxylamine soln. in methanolic NaOH is added and the mixture is held at 25° for 20 min. The soln. is then neutralised with 0·175 ml of 32% HCl and well shaken, and the NaCl is filtered off and washed twice with 1 ml of ether. The combined ether soln. are reduced to 0·75 ml, 0·2 ml of a 2% methanolic soln. of $FeCl_3$ is added and the volume is made up to 2 ml with methanol; 0·01 μl of this soln. is applied to paper for chromatography. This paper is impregnated with 2% methanolic ferric chloride soln. Ascending development with *n*-butanol - dimethylformamide - water (9:1:10) for 14 to 16 hr. is recommended. When the chromatogram is dried at 60°, the Fe^{III} - hydroxamic acid complexes are shown as violet spots on a yellow background. Fatty acid esters were detected by this method in oils of lavender, parsnip, heracleum (cow parsnip) and valerian. E. KAWERAU

2240. **New method for the determination of carvone and other ketones.** F. H. L. van Os and C. Scholtens. *Riechstoffe u. Aromen*, 1958, **8** (9), 265–268.—In a rapid colorimetric method for determining carvone (**I**) and other ketones, especially **I** in caraway oil, the max. extinction value is determined of the colour developed on treating the sample in ethanolic soln. with a soln. of ethyl 3:5-dinitrobenzoate (**II**) in methanol. The method gives results sufficiently accurate for practical purposes with simple soln. of **I** and with purified caraway oil, also with crude caraway oil if it is first treated with activated carbon to remove interfering impurities. *Procedure*—A 2% soln. of **II** in methanol (5 ml) is mixed with 4 ml of a soln. of the sample in methanol containing $\not<$ 1 mg of **I**; 1 ml of *N* NaOH is added, and the max. extinction of the colour developed after 1 min. is measured (over a period of 15 sec.) at 5375 A against a blank. Over the range of 5 to 40 mg of **I** the max. extinction rises linearly with the concn. of **I**. Crude caraway oils are first treated with $\simeq$ 0·5 g per 5 ml of activated carbon. H. L. WHITEHEAD

2241. **Determination of salicylanilide in varnishes by ultra-violet spectrophotometry.** M. H. Swann and M. L. Adams (Coating and Chem. Lab., Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1807–1808.—The salicylanilide is extracted from a solvent soln. of the varnish with NaOH soln. and the absorption is measured at 336 mμ; at this wavelength there is no interference from other varnish constituents. The recovery of added salicylanilide from tung-oil varnishes was > 99%. G. P. Cook

2242. **Test methods for chlorinated rubber.** P. F. Hover (Verfinst. T.N.O., Holland). *Verfkroniek*, 1958, **31** (6), 237–239.—Methods are described for the determination of H_2O, Cl, ash, pH, viscosity, tolerance for aliphatic hydrocarbons, and stability. L. A. O'Neill

2243. **Colorimetric determination of amine antioxidants.** C. L. Hilton. *Rubb. Age, N.Y.*, 1958, **84**, 263–267.—A method, based on a colour reaction obtained by coupling diazotised *p*-nitroaniline, is described for the qual. identification and determination of many of the more common amine antioxidants. The most satisfactory solvent system was found to be conc. HCl - methanol (1:3). The antioxidant is extracted from the sample, and an azo dye is formed by the use of the coupling agent. The intensity of the dye is measured spectrophotometrically. The antioxidant is identified by the colour. Rubber Abstr.

2244. **Determination of volatile *iso*cyanates from Desmophen - Desmodur paints.** W. Funke and K. Hamann (Forschungsinst. für Pigmente und Lacke, Stuttgart, Germany). *Farbe u. Lack*, 1958, **64** (3), 120–125.—The content of (tolylene) di*iso*cyanate in the atmosphere on application of paints based on Desmophens (polyesters) and Desmodurs (complex di*iso*cyanates) has been determined under conditions (*a*) in which the paints have been brushed out in a room under controlled ventilation conditions or (*b*) the paints have been applied to paper contained in a tube through which dry air was passed. Variations in the drying conditions and in the nature of the Desmodur were examined. The di*iso*cyanate was determined by the method of Ehrlicher and Pilz (*Arbeitsschutz*, 1956, 276; 1957, 7): the di*iso*cyanate was absorbed in aq. dimethylformamide - HCl, and hydrolysed to the diamine, which was diazotised, coupled with N-1-naphthylethylenediamine hydrochloride and determined colorimetrically. L. A. O'Neill

2245. **Determination of the metal content of paint driers. EDTA titration in alcohol - benzene solution.** C. A. Lucchesi and C. F. Hirn (Sherwin-Williams Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1877–1879.—The content of Ca, Co, Pb, Mn or Zn in a naphthenate or octoate drier can be determined in ≃ 10 min. by dissolution of the sample (0·2 g) in benzene - ethanol (1:25), followed by addition of 0·01 *M* EDTA (disodium salt) (40 ml) plus NH_4Cl - aq. NH_3 buffer (350 ml of conc. aq. NH_3 and 54 g of NH_4Cl diluted with water to 1 litre) (12 ml), and then back-titration of the excess of EDTA to the Eriochrome black T end-point. For Pb, tartaric acid, and for Mn, ascorbic acid (0·1 g) should be added before the titration. The coeff. of variation is ≃ 0·8% (10 analyses) and, compared with the gravimetric method, the relative accuracy is + 0·73% (Ca), − 0·49% (Co), − 0·24% (Pb), − 2·4% (Mn) and + 1·4% (Zn). W. J. Baker

2246. **Quantitative determination of tris(nonylated phenyl) phosphite (Polygard) in synthetic rubber and latex.** A. C. Nawakowski (Naugatuck Chem., Naugatuck, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1868–1872.—The two procedures described are based on the measurement of the phenolic fragments produced by alkaline alcoholysis of the phosphite, 2-ethoxyethanol being used as the alcohol. The alkylphenol produced can either be measured directly at 295 mμ or colorimetrically after being coupled with *p*-nitrobenzenediazonium fluoroborate. The coeff. of variation for the direct method is ± 0·04 to 0·06% and the concn. range is 0·057 to 0·085 g per litre; recoveries are > 90%. The colorimetric method has variable coeff. of variation of ± 0·008 to 0·025% and the concn. range is 0·010 to 0·030 g per litre; recoveries are > 95%. G. P. Cook

2247 **Determination of 2-nitrodiphenylamine in explosives.** L. Marvillet and J. Tranchant. *Mém. Poudres*, 1957, **39**, 329–331.—*Procedure*—Extract the explosive (5 g) for 48 hr. with dichloromethane. Evaporate the extract to dryness and dissolve in glacial acetic acid (50 ml). Add CCl_4 (25 ml) and 0·5 *N* brominated HBr (10 ml). Allow bromination to continue for 1 ± 0·25 min. and add conc. HCl (5 ml) and a 10% soln. of KI (25 ml). Titrate the soln. with 0·1 *N* $Na_2S_2O_3$ to starch. The method is specific even in the presence of significant quantities of nitroglycerin and phthalate. The limits of error are within ± 0·5%. K. R. C.

2248. **Analysis of explosives in non-aqueous media. Determination of diphenylamine and its derivatives.** L. Marvillet and J. Tranchant (Service des Poudres, France). *Chim. Anal.*, 1958, **40** (8), 293–298.—The classical bromination method for the determination of diphenylamine in explosives does not differentiate between diphenylamine and its nitroso derivatives and oxidation products. A titration in non-aq. media under the conditions described is unaffected by the presence of nitrocellulose, butyl phthalate, dinitrotoluene, 2-nitrodiphenylamine and nitrosodiphenylamine and gives a measure of the "free" diphenylamine in the sample. The finely ground sample (5 g) is dissolved in acetic acid (110 ml) and acetic anhydride (90 ml) and titrated potentiometrically with 0·01 *N* $HClO_4$ in acetic acid at 0°, with glass and silver - silver chloride electrodes. The end-point is deduced by inspection of the titration curve. W. T. Carter

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See also Abstracts—**2077**, Determination of CH_4 in carbon dioxide. **2112**, Determination of mixtures of H_2O_2 and peroxyacetic acid. **2113**, Determination of S^- in engine deposits. **2151**, Determination of oxalate. **2364**, Determination of CH_4 in coalmine air. **2365**, Colorimetric determination of diphenyl bases in air. **2374**, Determination of sulphates in fuels and coal. **2377**, Methylene blue method for determination of detergents. **2391**, Determination of S in fuel gas. **2399**, Chromatography of gas mixtures containing hydrocarbons. **2400**, Gas chromatograph as a methanometer in the coal industry. **2450**, $\beta\gamma$ Activity of tributyl phosphate soln.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

2249. **Determination of active blood volume with Evans blue, radioactive phosphorus-32 and chromium-51.** E. Wollheim, G. Becker and K. W. Schneider (Med. Univ.-klinik, Würzburg, Germany). *Klin. Wochschr.*, 1958, **36** (17), 800–808.—A modified method with Evans blue and a procedure for use with the radioactive isotopes ^{32}P or ^{51}Cr are described. Good agreement was obtained in a series of tests in which both types of method were used, and the accuracy of the more rapid dye method for routine use was established. The isotope method is of use chiefly in the clinical investigation of special cases. H. F. W. KIRKPATRICK

2250. **Polarographic determination of oxygen at pressures of over one atmosphere and its use for determining the oxygen consumption in biological experiments.** E. Schubert (Physiol. Inst. Univ., Leipzig, Germany). *Naturwissenschaften*, 1958, **45** (23), 571–572.—The whole apparatus is mounted inside a pressure chamber, only the polarographic leads issuing from it. As a measure of O consumption the diffusion current is measured whilst the potential of the cathode is constant (*e.g.*, — 0·6 V). The tissue is kept in fluid which is better than keeping it in air. The calibration curve is linear in regions above 100% of O (1 atm.).
E. KAWERAU

2251. **Determination of organic - inorganic ratio in osseous tissue by X-ray absorption.** G. P. Vose (Texas Woman's Univ., Denton, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1819–1821.—The mean absorption coefficient of osseous material varies in accordance with the wavelength of X-radiation and the relative proportions of organic and inorganic fractions in the absorbing mass; at constant wavelength the organic - inorganic ratio then establishes the mean absorption coefficient. For 1·5-g samples or less, the plot of transmittance *vs.* organic material (%) is linear. A precision of $\simeq \pm$ 1% was obtained from 10 determinations on a homogeneous mixture of human bone ash and casein. Good agreement was reached with values obtained by the dry ash method. G. P. COOK

2252. **Estimation of strontium in biological materials by means of a flame spectrophotometer.** G. E. Harrison (Med. Res. Council, Radiobiol. Res. Unit, Harwell, Berks., England). *Nature*, 1958, **182**, 792–793.—Determination of Sr by neutron activation is accurate but laborious. The flame-photometric method described is claimed to be rapid and accurate. Precipitate Ca and Sr oxalates from an HCl soln. of the material ashed at 650°, dissolve these in $\simeq$ 70% HNO_3 and precipitate the nitrates in $\simeq$ 90% HNO_3. The ppt. is dissolved in water and Sr determined at 460·7 mμ, slit width 0·05 mm, with an internal standard. An equation is given which makes allowance for interference from Ca. Results are compared with those from neutron activation; the error is 2 to 3% at Sr concn. of 2 p.p.m. P. D. PARR-RICHARD

2253. **Direct complexometric determination of calcium in serum with calcein as indicator.** H. Langendorf (Inst. f. physiol. Chem., Univ. Mainz, Germany). *Klin. Wochschr.*, 1958, **36** (17), 829–831.—Titration (*cf.* Baron and Bell, *Clin. Chim. Acta*, 1957, **2**, 327) can be carried out without pptn. or deproteinisation, and, by adjusting the pH to > 13, Mg is pptd. quantitatively as hydroxide. For the determination, 1 ml of serum is titrated with 0·002 *M* EDTA; alternatively, 0·5 ml of serum may be titrated with 0·0005 *M* EDTA.
H. F. W. KIRKPATRICK

2254. **Radiochemical analysis of strontium and barium in human urine.** L. B. Farabee (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Arch. Ind. Hlth*, 1958, **17**, 200–203.—A method is described for the determination of radioactive strontium and radioactive barium in human urine. The two nuclides are co-pptd. as their phosphates from alkaline soln. together with the phosphates of Ca and Mg. The ppt. is dissolved in HNO_3 and organic matter is destroyed by wet-ashing. The resulting ash is dissolved in HCl and the pH is adjusted to 9 with NaOH; the alkaline-earth ions are then chelated with EDTA (tetrasodium salt). Calcium and Mg are chelated preferentially to Sr and Ba. The mixture of chelates is next passed through a cation-exchange column and the adsorbed Ca and Mg are eluted with a mixture of citric acid and EDTA at pH 5. Sodium is removed by 0·5 *N* HCl and finally the Sr and Ba are eluted with 6 *N* HNO_3. The soln. is evaporated to dryness and aliquots of the mixture of Sr and Ba are counted by a conventional end-window Geiger - Müller counter.
NUTR. ABSTR. REV.

2255. **Determination of bicarbonate in plasma and its clinical significance.** M. Schwab and H. Wisser (Med. Univ.-Klinik, Göttingen). *Klin. Wochschr.*, 1958, **36** (16), 741–749.—A comparison of the results given by manometric and titrimetric methods showed no significant differences. The results are also in agreement with those deduced from pH and CO_2-tension measurements. The importance of the determination in disturbances of acid - base metabolism is discussed.
H. F. W. KIRKPATRICK

2256. **The chloramine-T method for the determination of nitrogen in plants.** Kh. N. Pochinok. *Biol. Fiziol. Rastenii*, 1958, (3), 53–59; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (2), Abstr. No. 1150.—The use of chloramine T instead of hypobromite in the determination of nitrogen in ashed plant material is investigated. It is shown that this simple method of determining the total and protein nitrogen replaces the Kjeldahl method with advantage. K. R. C.

2257. **Photometric micro-determination of vanadium, especially in biological material.** W. Pilz (Med. Dept., Farbenfabriken Bayer A.-G., Leverkusen, Germany). *Mikrochim. Acta*, 1958, (6), 789–802.—The prep. and purification of salicylhydroxamic acid for use in the determination of V present in aq. soln. are described. Although the colour intensity complies with the Lambert but not the Beer - Lambert law, a straight-line graph passing through the origin may be obtained by plotting the log. of the extinction against the concn. Foreign ions are removed and phosphates do not interfere and the method is specific for V in the range 1 μg to 2 mg. D. F. PHILLIPS

2258. **Determination of sulphur in plant materials.** O. A. Krober and R. W. Howell (Crops Res. Div., Agric. Res. Service, U.S. Dept. Agric., Urbana, Ill., U.S.A.). *J. Agric. Food Chem.*, 1958, **6** (8),

591–592.—The turbidimetric determination of S in plant materials is modified for rapid routine use by employing $Mg(NO_3)_2$ in the ashing process, which prevents loss of S and increases sensitivity, and by using a mixture of dipropylene glycol and ethanol (11:9) to improve the stability of the $BaSO_4$ suspension. If the transmittance is read at 720 mμ, it is seldom necessary to change the aliquot volume; for low concn. of S, greater sensitivity is possible at 410 mμ, though the aliquot volume must then be varied. M. D. ANDERSON

2259. **Determination of phenazone (antipyrin) in serum.** H. Nieth and P. Thiele (Med. Klinik d. Univ. Marburg a.d. Lahn, Germany). *Klin. Wochschr.*, 1958, **36** (17), 832–833.—The method in which the test soln. is treated with $NaNO_2$ and H_2SO_4 and the extinction read at 350 mμ or 366 mμ has been investigated with regard to the influence of temp. and $NaNO_2$ concn. The results indicate that an increase in temp. or concn. of $NaNO_2$ produces a very marked increase in the extinction. It is recommended that, to ensure reproducible results, 0·1 ml of 0·2% $NaNO_2$ soln. should be added to the test soln. and the extinction read after 60 min. at 20°. H. F. W. KIRKPATRICK

2260. **Chromatographic method for the determination of 4(5)-aminoimidazole-5(4)-carboxyamide and its content in human and animal urine.** A. E. Braunshteĭn and G. Ya. Vilenkina (Acad. Med. Sci., Moscow). *Biokhimiya*, 1958, **23** (6), 887–890.—The importance of an internal standard of 4(5)-aminoimidazole-5(4)-carboxyamide (**I**) is stressed. Conc. HCl (2 to 3 ml) is added to a urine sample which is made up to 50 ml and extracted with peroxide-free ether for 10 min. The aq. phase is neutralised with Na_2CO_3. A mixture consisting of anhyd. Na_2SO_4 and $Na_3PO_4.H_2O$ (6:1) (2 g), is added to an aliquot (10 ml) followed by *n*-butanol (10 ml). The internal standard soln. (0·1 ml) (6 mg of synthetic **I** in 100 ml of 50% methanol) is added to two assays. The air in the dark-glass containers is replaced by nitrogen, and the containers are agitated for 30 min. The *n*-butanol layer is separated by centrifuging. The aq. phase is re-extracted with *n*-butanol. The combined butanolic phases are shaken with 0·5 *N* HCl (5, 3, 3 ml); the aq. phase separates on standing. The combined aq. phases are evaporated to dryness under vacuum in an atmosphere of nitrogen. The residue is dissolved in methanol (0·2 ml), and filter-paper, which has received a preliminary washing with a 0·5% soln. of EDTA, is spotted with 40-μl aliquots. The solvent used is *n*-butanol saturated with 10% aq. NH_3 soln. After developing the chromatogram for 16 to 18 hr., the spots are revealed by u.v. irradiation. The strips are sectioned and passed through a chilled soln. of diazobenzenesulphonic acid. Excess of reagent is removed, and the colour is fixed by washing with ethanol (96%). The blue spots are extracted with 10% aq. NH_3 soln. (3 ml), and the extinction is measured at 570 mμ. A 1-μg amount can be determined with an accuracy of ± 10%. With larger quantities the accuracy is correspondingly greater. The content of **I** in the urine of man, rabbit and dog was determined. Inhibition of intestinal flora with antibiotics does not affect the content in rat urine, but a subcutaneous injection of aminopterin augments it considerably.
K. R. C.

2261. **Determination of glucose in biological fluids with ethylenediaminetetra-acetic acid.** H. V. Street (Dept. of Pathology, Crumpsall Hospital, Manchester, England). *Analyst*, 1958, **83**, 628–634.—The procedure is suitable for blood, diluted urine and cerebrospinal fluid. The sample (0·2 ml) is added to 1·6 ml of a Na_2SO_4 - Na_2WO_4 reagent and after 5 min. 0·2 ml of 0·33 *N* H_2SO_4 is added. After centrifuging, 1 ml of the supernatant liquid is added to 1 ml of an alkaline copper reagent. A blank soln. is prepared by mixing 1-ml portions of water and copper reagent and also a standard soln. (≡ 100 mg of glucose per 100 ml) by mixing 1-ml portions of a standard glucose soln. and the copper reagent. The tubes containing the liquids are placed in boiling water for exactly 5 min. and then cooled in water. Murexide indicator is added and the liquids are titrated with 0·005 *M* EDTA (disodium salt) to a violet end-point. From the titres of the blank, standard and sample soln. the glucose content of the sample is calculated. Recovery experiments showed that amounts of glucose up to 400 μg can be recovered from urine with an error of ± 2%. A. O. JONES

2262. **Separation of glucose 1-phosphate and glucose 6-phosphate by paper chromatography.** F. E. G. Harrap (Lessington Res. Sta., Ipswich, Suffolk, England). *Nature*, 1958, **182**, 876.—Addition of boric acid to saturate 2-methoxyethanol - ethyl methyl ketone - 3 *N* aq. NH_3 (7:2:3) gives a sharp separation of glucose 1-phosphate from glucose 6-phosphate, fructose 1:6-diphosphate and inorganic orthophosphate.
H. F. W. KIRKPATRICK

2263. **Uronic acid determination.** S. A. Barker, A. B. Foster, I. R. Siddiqui and M. Stacey (Chem. Dept., Univ., Birmingham, England). *Talanta*, 1958, **1** (3), 216–218.—The determination by decarboxylation is independent of the nature of the uronic acid present. Modifications to the apparatus of McCready *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 290) enable 20-mg samples to be used. These are decarboxylated with 19% HCl and the CO_2 is absorbed in standard NaOH soln. and back-titrated with HCl. *Procedure*—To the sample in a flask add 3 ml of 19% HCl and sweep with N. Add 5 ml of 0·25 *N* NaOH to an absorption tube (CO_2-free) and connect to the flask through a water condenser and zinc-filled trap. Heat at 145° for 2 hr. under N, then sweep with an increased flow of N (2 to 3 bubbles per sec.). Transfer the contents of the tube to a flask, add 2 ml of 10% $BaCl_2.2H_2O$ soln. and two drops of phenolphthalein and titrate with 0·1 *N* HCl under N.
P. D. PARR-RICHARD

2264. **Determination of chlorogenic acid and caffeic acid by means of paper chromatography.** G. Giovannozzi-Sermanni (Univ., Perugia, Italy). *Ric. Sci.*, 1958, **28** (9), 1871–1873.—A method is given for the determination of chlorogenic acid by paper chromatography. The results of the determination of caffeic acid in a sample of tobacco are given. C. A. FINCH

2265. **Colorimetric test for gibberellic acid and evidence from a dwarf-pea assay for the occurrence of a gibberellin-like substance in wheat seedlings.** G. M. Simpson (Wye College, nr. Ashford, Kent, England). *Nature*, 1958, **182**, 528–529.—Extracts from wheat seedlings were chromatographed with *iso*propyl alcohol - aq. NH_3 (0·880) - H_2O (10:1:1)

as developer, and eluted with acetone. Two-dimensional chromatograms of these eluates gave negative results when sprayed with Folin and Ciocalteu's reagent [lower limit 5 μg of gibberellic acid (**I**)]. **I** in the same solvent systems gave two blue spots with the reagent; an acetone extract of the area of original paper corresponding to the first of these spots stimulated dwarf-pea-seedling growth to a degree equiv. to < 1 μg of **I**. Statistical analysis shows significant activity in two of the extracts from wheat seedlings.

P. D. PARR-RICHARD

2266. **Investigation of the staining of isolated serum lipids and its significance in lipid electrophoresis.** G. Berg, F. Scheiffarth, C.-J. Estler and H. Schön (Med. Univ.-Klinik, Erlangen, Germany). *Klin. Wochschr.*, 1958, **36** (16), 766–769.—Total lipids were extracted from serum and fractionated on a silica column. The lipid fractions were stained with Sudan black B after paper electrophoresis and the colours measured in a scanner. Each fraction was found to take up a different proportion of dye and it is concluded that quant. evaluation of the lipid fractions after electrophoresis by this means is invalid. H. F. W. KIRKPATRICK

2267. **Infra-red spectra of sialic acids and sialic acid methyl esters.** I. Fischmeister (Inst. Med. Chem., Univ. of Uppsala, Sweden). *Ark. Kemi*, 1958, **13** (3), 247–258.—The i.r. spectra of porcine (P), ovine (O), equine (E) and bovine (B) sialic acids, methoxyneuraminic acid and the methyl esters of O- and P-sialic acids are reproduced and their differences reported. For comparison, i.r. spectra of certain sugars (glucose, galactose, N-acetylglucosamine, N-acetylgalactosamine, glucosamine hydrochloride and galactosamine hydrochloride) are also reproduced. A double-beam spectrometer and the potassium bromide disc technique were used. The spectral range covered is 2·5 μ to 15 μ. The accuracy in position of absorption max. is said to be $\pm$ 0·015 μ. For identification purposes the following characteristic absorption bands are proposed—P-sialic acid, the strong absorption at 8·3 μ; O-sialic acid, the four absorption bands with regularly decreasing intensities from 7·8 μ to 8·4 μ; E-sialic acid, the strong absorption at 7·09 μ; B-sialic acid, position of amide bands and the strong absorption at 13·72 μ. The wavelengths of max. absorption in the i.r. spectra of four sialic acids, two sialic acid methyl esters and of methoxyneuraminic acid are tabulated.

B. RÖNNHOLM

2268. **Quantitative paper-chromatographic determination of folic acid in urine after folic acid loading.** R. Hähnel (Hautklinik d. Martin-Luther-Univ., Halle, Germany). *Klin. Wochschr.*, 1958, **36** (17), 828–829.—The patient is given 100 mg of folic acid orally, and urine is collected at 2, 5, 9, 13 and 24 hr. The vol. of each sample is measured and aliquots (2 ml) are treated with H_2O (5 ml), 2·5 *M* acetate buffer, pH 3·95 (0·1 ml), and 6% $KMnO_4$ soln. (0·5 ml). After setting aside the mixture for 1 hr. at room temp., acetate buffer (0·1 ml) and 30% H_2O_2 (a few drops) are added to give a clear colourless soln., which is made up to 10 ml. An aliquot (0·1 ml) is chromatographed on paper with *n*-butanol - acetic acid - water (4:1:5) as solvent; when the solvent front has travelled 60 to 80 cm the paper is removed and dried at 100° for 30 min. The oxidation product of folic acid is located as a blue fluorescent spot in u.v. light; this is cut out and extracted with H_2O (10 ml) for 30 min. and the fluorescence is measured in a fluorimeter. Standard soln. of folic acid (20 to 500 μg in 10 ml) are treated in the same way. H. F. W. KIRKPATRICK

2269. **Determination of 4-pyridoxic acid in human urine.** S. K. Reddy, M. S. Reynolds and J. M. Price (Sch. of Home Economics, Univ. of Wisconsin, Madison, U.S.A.). *J. Biol. Chem.*, 1958, **233** (3), 691–696.—4-Pyridoxic [3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxylic] acid is determined fluorimetrically after the removal of interfering fluorescent compounds by ion-exchange chromatography on Dowex 1 (Cl^-) and Dowex 50 (H^+). After elution of the acid with 2 *N* HCl, the determination is carried out in four steps, (*i*) delactonisation by heating with aq. NaOH soln., (*ii*) lactonisation by heating with aq. HCl, (*iii*) adjustment of pH to 9·0 $\pm$ 0·3 and dilution, and (*iv*) determination in a Coleman 12 photofluorimeter with filters B-1 and PC-1. The amount of acid is ascertained from a standard graph. The method is applicable to human urine samples that contain more than 2 μmoles of 4-pyridoxic acid per 24 hr.

J. N. ASHLEY

2270. **Fluorimetric estimation of epinephrine [adrenaline] and norepinephrine [noradrenaline].** R. T. Jones and W. D. Blake (Univ. of Oregon Med. School, Portland, U.S.A.). *J. Appl. Physiol.*, 1958, **12** (3), 448–452.—Factors leading to unreliable results in the application of the Lund fluorimetric method (*Acta Pharm. Tox., Kbh.*, 1949, **5**, 231) to the assay of adrenaline and noradrenaline in urine and plasma have been examined. Careful selection of reagents and conditions is necessary. Treatment with Al_2O_3 alters the fluorescence produced by subsequent oxidation with MnO_2, the amount of change depending on the pH at which the oxidation is carried out; thus the apparent recovery of adrenaline is altered. A significant increase in noradrenaline concn. in urine has been observed after several days' storage, but adrenaline appears to be relatively stable in urine and plasma.

D. W. Moss

2271. **Determination of free amino acids in cerebrospinal fluid and their clinical significance.** H. G. Knauff, W. Mialkowsky and H. Zickgraf (Med. Klin., Univ., Munich). *Klin. Wochschr.*, 1958, **36** (15), 739–740.—High-voltage electrophoresis followed by paper chromatography showed the regular occurrence of 25 ninhydrin-positive substances. No significant differences in the amino-acid distribution were observed between normal and pathological fluids, and it is concluded that their determination is of little clinical value.

H. F. W. KIRKPATRICK

2272. **Direct photometry of paper chromatograms with the aid of a simple extinction recorder. Quantitative determination of amino acids.** J. Barrollier, J. Heilmann and E. Watzke (Schering A.-G., W. Berlin, Germany). *J. Chromatography*, 1958, **1** (5), 434–445 (in German).—An apparatus is described for the automatic production of extinction curves from chromatograms and electropherograms. The adjustment of the mirror so that the reflected beam of a mirror galvanometer traces the extinction curve is made with the aid of an optical wedge, the construction of which is described. The determination of amino acids is described as an example of its use. G. BURGER

2273. **Quantitative estimation of amino acids by paper chromatography.** A. F. S. A. Habeeb (The Sterling Chem. Lab., Yale Univ., New Haven, Conn., U.S.A.). *J. Pharm. Pharmacol.*, 1958, **10** (9), 591–592.—The method of Levy (*Anal. Abstr.*, 1954, **1**, 2772) is modified as follows. Allow the amino acids (20 μmoles of each) to react with 1-fluoro-2:4-dinitrobenzene for 1·5 or 2 hr. in 0·1 *N* aq. KCl, and subject the dinitrophenylamino acids to two-dimensional paper chromatography with ethylbenzene - *tert.*-amyl alcohol - 1·6 *N* aq. NH_3 (1:3:2) as solvent in one direction followed by 1·5 *M* phosphate buffer in the other direction. Results are reproducible within ± 5%, and for β-lactoglobulin compare favourably with those reported elsewhere. A. R. ROGERS

2274. **Experiences with the plate assay of L-phenylalanine with a mutant of *Escherichia coli*.** L. Dickinson (Boots Pure Drug Co. Ltd., Nottingham, England). *Analyst*, 1958, **83**, 647.—A valine-resistant mutant of *E. coli* was maintained on nutrient agar slopes (prep. described). The inoculum was prepared from a 24-hr. culture in Lemco broth. Cups were filled and the Petri plates were incubated for 48 hr. at 37°. When L-phenylalanine was assayed in the presence of 0·2% of casein hydrolysate the zones were smaller than those of standards in water. Phenylalanylglycine and glycylphenylalanine gave zones equiv. to their phenylalanine content. D-Phenylalanine gave zones only at much higher concn. The plate assays of cell extracts always gave lower results than dilution assays with the *E. coli* mutant in lactate medium. The plate assay is less sensitive than the dilution test, but is less laborious. A. O. JONES

2275. **Experiences with the plate assay of L-phenylalanine with a mutant of *Escherichia coli*.** A. Jones and S. M. Burns (Beecham Maclean Ltd., Lucozade Annexe, Great West Rd., Brentford, Middx., England). *Analyst*, 1958, **83**, 648–649.—With the medium described by Dickinson (*Ibid.*, 1958, **83**, 647) indistinct zones were obtained with a new culture of the mutant. Difficulties were encountered with the inoculum. A 24-hr. culture grown at 37° often gave hazy zones, one grown for 48 hr. at the same temp. gave sharp zones, but the sharpest zones were obtained with a basal medium containing casein hydrolysate. Preparation of stock cultures of the mutant and suspensions of the inoculum are described as well as the preparation of the assay medium. Recoveries of L-phenylalanine added to casein hydrolysate were 85 to 115% when the proportion (w/w) of L-phenylalanine to hydrolysate varied from (1:1) to (1:200). When samples were assayed by both the plate method with *E. coli* and the tube method with *Leuconostoc mesenteroides* P60 good agreement was obtained with hydrolysates containing 0·3 to 6·0% of L-phenylalanine. A. O. JONES

2276. **Assay of some sulphydryl compounds.** K. J. Steel (School of Pharmacy, Univ. of London). *J. Pharm. Pharmacol.*, 1958, **10** (9), 574–576.—Dissolve the sample of thioglycollic acid (0·3 g) in H_2O (20 ml), add glacial acetic acid (2 ml) and KI (0·2 g) and titrate with *M*/60 KIO_3. This method of assay is more reproducible than that of the B.P. 1958, and it is thought to be more accurate. Cysteine hydrochloride, dimercaprol and glutathione may be assayed similarly. A. R. ROGERS

2277. **Oxidation of methionine with hydrogen peroxide vapour: its application in paper-chromatographic analysis of the amino acid.** J. Datta, K. R. Bhattacharya, A. Sen and D. K. Roy (Indian Inst. Biochem. Exp. Med., Calcutta). *Ann. Biochem. Exp. Med.*, 1957, **17**, 211–214.—Filter-paper with a spot of an amino-acid mixture was left inside a glass jar previously saturated with H_2O_2 vapour for about 6 hr. Methionine was oxidised to methionine 5-oxide and could then be easily separated from other amino acids by chromatography. NUTR. ABSTR. REV.

2278. **Specific identification of hydroxyamino acids on paper chromatograms of protein hydrolysates.** D. P. Schwartz (U.S. Dept. Agric., Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1855–1856.—A test for serine is based on the condensation of the formaldehyde, liberated by action of HIO_4 on serine, with acetylacetone to form the yellow, highly fluorescent 3:5-diacetyl-1:4-dihydrolutidine. Hydroxylysine, found only in a few proteins, also gives a positive response. A test for threonine in the presence of all amino acids is based on the reaction of acetaldehyde with sodium nitroprusside and piperidine after oxidation with HIO_4. G. P. COOK

2279. **Determination of free formaldehyde in the presence of amino acid - formaldehyde and protein - formaldehyde compounds.** M. Ya. Fel'dman (Anti-Polio. Res. Inst., Moscow). *Biokhimiya*, 1958, **23** (6), 917–923.—A diffusion method is used to determine free formaldehyde in aq. soln. in the presence of formaldehyde reversibly combined with proteins, amino acids and other compounds. The method consists in gas diffusion from a relatively large vol. (20 ml) of test soln. into a very small vol. (0·3 ml) of water or buffer soln. at the pH of the test soln., until equilibrium is reached. Hermetically sealed, modified Conway cups are used and the test soln. is placed in the outer chamber. After 48 hr., free formaldehyde is determined in the absorbing soln. of the inner chamber by the method of Tannenbaum and Bricker (*Anal. Chem.*, 1951, **23**, 354). Recoveries of 99·8 ± 2·8% were obtained after 48 hr. K. R. C.

2280. **Assay of aromatic amino-acid transaminations and keto-acid oxidation by the enol borate-tautomerase method.** E. C. C. Lin, B. M. Pitt, M. Civen and W. E. Knox (Dept. of Biol. Chem., Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Biol. Chem.*, 1958, **233** (3), 668–673.—Continuous spectrophotometric assays are described for five enzymes which either form or break down aromatic or heterocyclic α-keto acids. The assays are based on the keto - enol tautomerism and the u.v. absorption in the 300-mμ region of the enol borate complexes of the keto acids. Optimum conditions are given for the assay of these enzymes in crude liver extracts or in partly purified preparations. J. N. ASHLEY

2281. **Colorimetric determination of amino-oxy acids.** Y. Knobler and M. Weiss (Dept. Org. Chem., Hebrew Univ., Jerusalem). *Experientia*, 1958, **14** (9), 332.—This method is based on the orange colour reaction given by amino-oxy compounds on the addition of alkaline picrate. The reaction has been developed for the determination of canaline, amino-oxyacetic acid and hydroxylamine. The optical density is measured at 525 mμ, 5, 7 and 9 min. after the addition of saturated aq.

picric acid and 1% NaOH soln., the average value of the readings serving as the figure taken for the determination of the amino-oxy compound by reference to a calibration curve. From 0·5 to 7·0 μmoles per ml may be determined by this procedure.
P. NICHOLLS

2282. **Determination of proteins by the xantho-protein reaction.** L. M. Buruiana (Lab. Biochem. Animal., Fac. Med. Vet., Bucharest, Romania). *Naturwissenschaften*, 1958, **45** (14), 339–340 (in French).—The reaction mixture consists of 0·1 ml of whole or diluted milk to which 1 ml of HNO_3 ($d = 1{\cdot}40$) is added. The mixture is boiled over an open flame for 5 to 15 sec. It is cooled and kept under running cold water whilst being neutralised with 30% NaOH soln., the end-point being recognised by the change in colour. The mixture is now diluted to 5 or 10 ml and filtered; the colour intensity of the filtrate is then measured in a photoelectric colorimeter, with a blue filter having an optimum transmission at 430 mμ. The Beer-Lambert law is obeyed over a wide range (25 to 3000 μg of protein). A calibration curve should be constructed from parallel determinations by the Kjeldahl method. The method is applicable to serum proteins.
E. KAWERAU

2283. **Investigation of the specificity and quantitative value of precipitation of γ-globulin in cerebrospinal fluid with zinc sulphate.** D. Pette (Neurolog. Klinik, Univ., Hamburg). *Klin. Wochschr.*, 1958, **36** (16), 775–777.—Electrophoretic patterns of the c.s.f., the ppt. with $ZnSO_4$, and the supernatant fluid from the pptn. showed no significant differences. The test with $ZnSO_4$ is therefore of no value in measuring the γ-globulin.
H. F. W. KIRKPATRICK

2284. **Rapid electrophoretic separation of haemoglobins and serum proteins.** B. Zak and T. L. Jarkowski (Wayne State Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Clin. Chim. Acta*, 1958, **3** (5), 494–496.—The agar procedure previously described by Zak and Sun (*Amer. J. Clin. Path.*, 1958, **29**, 69) is modified by shortening the plate from 13 to 4 in. and applying 250 V as before, thus increasing the potential gradient. The test run is reduced from 3 to 4 hr. to 30 to 45 min.
H. F. W. KIRKPATRICK

2285. **Rapid method for the determination of the radioactivity of proteins and the relative proportions of various radioactive fractions in plant leaves.** Zh. A. Medvedev (Timiryazev Acad. of Agric. Sci., Moscow). *Biokhimiya*, 1958, **23** (6), 801–808.—Leaves between double layers of filter-paper are subjected to a pressure of 25 to 100 kg per sq. cm. The dried papers are sprayed with trichloroacetic acid (10%) and then washed several times with a weaker soln. (2 to 3%). Final washings are made on Büchner funnels. Nucleic acids will dissolve if hot instead of cold trichloroacetic acid is used in the washing process. Lipids and plastid pigments are eliminated by Soxhlet extraction with ethanol and ether. The residual proteins are then determined gravimetrically for a unit surface-area. Their specific activity is calculated from the surface radioactivity of the leaf impressions. The relative proportions of various radioactive substances are determined by measuring the surface activity at different stages of the washing operation. Results of certain tests are given.
K. R. C.

2286. **Recognition and estimation of denatured deoxyribonucleate.** J. Shack (Nat. Cancer Inst., Nat. Inst. of Health, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1958, **233** (3), 677–680.—A spectrophotometric method is described for the determination of denatured deoxyribonucleic acid in the presence of the native acid. It depends on the reversible changes in the u.v. absorption of the denatured nucleic acid with changes in temp. and in the concn. of NaCl. Some of these changes occur in a range of conditions in which the u.v. absorption of the native material is independent of the concn. of NaCl and practically independent of temp.
J. N. ASHLEY

2287. **The infra-red spectra of 5-hydroxymethyluracil and nucleic acid pyrimidines.** T. L. V. Ulbricht (Dept. Pharmacol., Yale Univ. School of Medicine, New Haven, Conn.). *Naturwissenschaften*, 1958, **45** (17), 416–417.—The infra-red spectrum of 5-hydroxymethyluracil (**I**) is compared with those of uracil, thymine, cytosine and 4-amino-5-hydroxymethyl-2-methylthiopyrimidine. The distinguishing features of the spectra are fully discussed and they confirm the structure of **I**. The method is suitable for distinguishing these substances when present in micro quantities.
E. KAWERAU

2288. **Oscillographic polarography of the nucleic acids and their constituents.** E. Paleček (Biophys. Inst., Czech. Acad. Sci., Brno). *Naturwissenschaften*, 1958, **45** (8), 186–187.—Five of the constituent purine and pyrimidine bases give characteristic patterns. Adenine, guanine and cytosine can be determined in the free state or bound as nucleosides or nucleotides. Adenine in 2 *N* H_2SO_4 or dissolved in glacial acetic acid can be detected in concn. as low as 0·4 μg per ml. Uracil and thymine can be detected only in an alkaline medium. In the presence of KCl, deoxyribonucleic acid (**I**) and ribonucleic acid give distinctive patterns. **I** reacts with cobalt and nickel, thus enabling **I** and protein to be determined simultaneously.
E. KAWERAU

2289. **Rapid and sensitive method for the determination of total serum cholesterol.** J. G. Hauge and R. Nicolaysen (Johan Throne Holst's Inst. f. Ernœringsforsking, Univ., Oslo). *Acta Physiol. Scand.*, 1958, **43** (3–4), 359–364 (in English).—The method described is a combination of the $CHCl_3$ extraction procedure of the Kingsley and Schaffert version of the Liebermann-Burchard reaction (*Brit. Abstr. C*, 1950, 65) with the sensitive colour reaction of the Tschugaeff and Görtz test as modified by Hanel and Dam (*Anal. Abstr.*, 1955, **2**, 3160). A preliminary saponification of the sample is included to prevent material from sticking to the glass walls and thus remaining unextracted.
A. TESSLER

2290. **The oscillopolarography of steroids.** V. Moravek (Biochem. Inst. Naturwissenschaftlich. Fakultät, Masaryk Univ., Brno, Czechoslovakia). *Naturwissenschaften*, 1958, **45** (23), 571.—The estimations are carried out in an *iso*propyl alcohol-HCl soln. with either a dropping or streaming mercury electrode. Quant. determinations can be carried out on concn. down to 10^{-4} mole per ml. Steroids possessing a hydroxyl or ester group at C_3 show a double peak on the cathode picture when the streaming electrode is used, whereas steroids having a keto group show a treble peak. With the dropping mercury electrode the oscillograms are

of different appearance, their heights depending on the presence or absence of hydrated A or B rings, a substituent group on C_{17} or a keto group on C_3.
E. KAWERAU

2291. **A new method for the determination of steroids having a Δ^4-3-keto group with blue tetrazolium.** H. Dowlatabadi (21, Azar Avenue, Theran, Iran). *Naturwissenschaften*, 1958, **45** (21), 517–518.—Blue tetrazolium reacts with these reducing steroids in aq. soln. to yield a yellow colour which has a maximum absorption at 377 mμ and obeys the Beer - Lambert law. The colour is stable for at least 12 hr. and can be used for the quant. determination of these steroids. A standard curve is prepared by dissolving 20 mg of the steroid in 100 ml of methanol. Aliquots of this soln. are measured into glass-stoppered tubes and the volume is made up to 2 ml with methanol; 1 ml of aq. blue tetrazolium is added to each tube followed by 2 ml of 2 *N* NaOH. The tubes are now incubated for 40 min. in a water bath at 40°. The extinction values are then read in a spectrophotometer at 380 mμ against a reagent blank. The unknown soln. are treated in the same way. E. KAWERAU

2292. **Qualitative, quantitative and preparative chromatography of steroids on fully acetylated paper. I. Qualitative chromatography of Δ^4- and $\Delta^{1,4}$-3-oxosteroids.** F. J. Ritter and J. Hartel (Central Lab. T.N.O., Delft, The Netherlands). *J. Chromatography*, 1958, **1** (5), 461–470.—Fully acetylated paper, being more nearly homogeneous, yields better reproducibility than partly acetylated paper. The method of preparation is described. The chromatograms are sharpened by sewing a strip of un-acetylated paper along the bottom. Three procedures are described. (*i*)—The chromatogram is run with a single-phase mixture of benzene, methanol and water (1:10:3) for 5 hr. without previous equilibration of the paper. (*ii*) and (*iii*)—A two-phase mixture of benzene, methanol and water (4:4:1) is used. In (*ii*) the lower phase is used for equilibration of the paper for 16 hr. and the upper phase as the mobile phase, and vice versa for (*iii*). The spots can be detected by examination by Bush's method (spraying with 10% NaOH soln. in 60% ethanol and viewing under u.v.) or by treatment with alcoholic 2:4-dinitrophenylhydrazine. Ketosteroids from C_{18} to C_{27}, including sex hormones and adrenal cortex hormones, have been separated. G. BURGER

2293. **The use of triethylene glycol as the stationary phase in the chromatographic separation of 17-oxosteroids.** L. Stárka and J. Živný (ForschInst. f. Endokrinologie, Prague, Czechoslovakia). *Naturwissenschaften*, 1958, **45** (23), 570–571.—The test soln. is applied to Whatman No. 1 paper and dried. The paper is then impregnated with 30% triethylene glycol in methanol and the paper dried by blotting. After 20 min. the paper is hung in a chamber which is saturated with the vapour of the mobile phase. The paper is now developed by a descending run with light petroleum for 2 to 3 hr. The solvent front has travelled 30 to 35 cm in this time. The steroids are identified by the Zimmermann reaction which shows considerably increased sensitivity in the presence of triethylene glycol, as little as 0·1 μg of dehydro*epi*androsterone being detectable. The present system is particularly suitable for the separation of dehydro*epi*androsterone, *epi*androsterone and androsterone. R_F values for 18 steroids are given. E. KAWERAU

2294 **Estimation of 17:21-dihydroxy-20-oxosteroids in plasma by a micro-modification of the Porter - Silber assay.** A. M. Riondel, M. C. Sanz and A. F. Muller. *Acta Endocrinol.*, 1957, **26**, 57–64.—This method is claimed to have all the advantages of the original method (*cf.* Silber and Porter, *Anal. Abstr.*, 1955, **2**, 142) but requires only 2 ml of plasma. *Procedure*—To 2 ml of heparinised plasma add 1 μg of cortisol to raise extinctions which are otherwise too low. Shake vigorously with 10 ml of $CHCl_3$ for 20 sec. and then centrifuge. Transfer the centrifuged $CHCl_3$ extract to another tube and wash with 0·1 *N* NaOH (0·4 ml) by shaking for 15 sec. Centrifuge briefly and remove the alkaline wash with a capillary tube. Divide the washed $CHCl_3$ extract into two 4-ml aliquots; to one, add 0·5 ml of ethanolic phenylhydrazine - sulphuric acid reagent, and use the other 4 ml as a reagent blank. Shake the tubes for 2 min. and then centrifuge. Transfer the supernatant reagent layer to a 1·5-ml test-tube. Heat in a water bath at 60° for 30 min., cool and transfer the soln. to micro-cells. Read the extinctions at 370, 410 and 450 mμ. Prepare standards by adding 0·5, 1·0, 1·5 and 2·0 μg of cortisol in water to four 2-ml plasma samples previously washed with $CHCl_3$, and treat as samples.
B. P. BLOCK

2295. **New systems for the separation of corticosteroids by paper chromatography.** M. Prusíková (ForschInst. f. Endokrinol., Prague, Czechoslovakia). *Naturwissenschaften*, 1958, **45** (19), 466–467.—A fraction of the urinary extract corresponding to one-fortieth to one-twentieth of the 24-hr. volume, or a soln. of the pure steroid (≡ 10 to 20 μg), is applied to Whatman No. 1 paper and dried. The paper is now passed through a 30% soln. of ethanediol in methanol and dried between a double layer of filter-paper. The chromatogram is hung in a vessel saturated with CCl_4 vapour and developed for 10 hr. with CCl_4 which has been saturated with either ethanediol or propanediol. The system is useful for separating aldosterone from other urinary corticosteroids. R_F values for corticosteroids and their acetates are given. E. KAWERAU

2296. **Separation of mixtures of oestrogens in urinary extracts using gradient elution chromatography.** S. Kushinsky, J. A. Demetriou, W. Nasutavicus and J. Wu (Univ. of S. Calif. Sch. of Med., Los Angeles, U.S.A.). *Nature*, 1958, **182**, 874–875.—The oestrogens, adsorbed on silica gel, are eluted with progressively increasing concn. of ethyl acetate in benzene. A suitable apparatus is indicated for producing a linear concn. gradient. Results of typical separations are given.
H. F. W. KIRKPATRICK

2297. **Assay of thrombin preparations.** E. Jorpes, T. Vrethammar, B. Öhman and B. Blombäck (Chem. Dept. II, Karolinska Inst., Stockholm, Sweden). *J. Pharm. Pharmacol.*, 1958, **10** (9), 561–573.—The relative strength of three commercial thrombin preparations has been compared with that of an arbitrary standard. Heparinised plasma and toluene-*p*-sulphonyl-L-arginine methyl ester are both unsuitable as clotting substrates. Fibrinogen prepared by the method of Blombäck and Blombäck (*Ark. Kemi*, 1956, **10**, 415) can be used. The potencies were estimated by comparison of the rates of clotting of the substrate; the 95% fiducial limits of error in two experiments were 97 to 103% and 94 to 107%, respectively. Thrombin preparations may also be assayed by measurement

of the rate of appearance of N-terminal glycine in the fibrinogen soln. (*cf.* Blombäck, *Ark. Kemi*, 1958, **12**, 173). A. R. ROGERS

See also Abstracts—**2232**, Determination of polynitro compounds in urine or serum. **2234**, Detection limits of flavones. **2308**, Determination of hypericin, rutin and quercetin in *Hypericum*. **2310**, Assay of cellulases. **2353**, Separation of unsaturated fatty acids from lipids. **2374**, Determination of sulphates in biological materials. **2402**, Apparatus for electrophoresis of proteins.

Pharmaceutical analysis

2298. **Determination of alkaloids by means of paper chromatography. I.** J. Büchi and H. Schumacher (Pharm. Inst., ETH, Zürich). *Pharm. Acta Helv.*, 1958, **33** (7), 274–286.—Previous work is discussed, and measurement of spot area is claimed to be superior to other methods of determination. A linear relationship is shown to exist between spot area, as found by use of squared mm paper, and weight of alkaloid, and a method for the separation and estimation of mixtures of strychnine and brucine is proposed. By using sample weights of 25 μg to 100 μg an accuracy of $\pm$ 2% is claimed. The sample in $CHCl_3$ is applied to a starting line in the form of three drops of equal volume. Three drops of a standard soln. containing more alkaloid than expected, and three with less, are also applied. The paper is developed with *iso*butyl alcohol - toluene, saturated with water and buffered to pH 6·6, and is dried. The spots are rendered visible by spraying with Dragendorff reagent. The R_F value of brucine is 0·39, and that of strychnine is 0·61. The mean spot areas of the standards are found and used to prepare a standard curve, from which the amount of alkaloid can be found. Various methods for the analysis of *Strychnos nux-vomica* seeds are discussed. The method of Pharmacopoeia Helvetica V, and the separation method of Eder and Ruckstuhl (*Ibid.*, 1944, **19**, 23) give inaccurate results, which are thought to be due to oxidation of the alkaloids. H. M.

2299. **Amperometric titrations of organic bases. VI. The use of nitranilic acid as titrant.** J. Kráčmar and J. Zýka (Dept. of Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1958, **7** (5), 246–249.—Various organic bases were titrated with 0·1 *N* nitranilic acid in 0·01 *N* KCl at $-$ 0·5 V *vs.* the S.C.E. For quinine, cinchonine, strychnine and some antihistamines the method was successful. In other cases a considerable error due to a relatively high solubility of the resulting salt was observed. J. VOLKE

2300. **Determination of brucine by polarography and oscillopolarography.** G. Dušinský (Res. Inst. Pharm. Ind., Bratislava, Czechoslovakia). *Acta Chim. Acad. Sci. Hung.*, 1958, **16** (3), 351–361 (in German).—Brucine can be determined in the presence of strychnine and some other alkaloids, by quant. conversion (with 4 *N* HNO_3) into *o*-brucinequinone which is then reversibly reduced polarographically ($E_{\frac{1}{2}} = -$ 0·2 V at pH 7). Cacotheline shows a second irreversible step corresponding to reduction of the NO_2 group. Since this second wave does not interfere, brucine can be determined polarographically in the presence of easily nitrated compounds. The error is $\simeq \pm$ 1%. The oscillographic method (*cf.* Heyrovský, *Anal. Abstr.*, 1955, **2**, 3547) is more rapid, but is accurate only for soln. of pure brucine. The lower limit of determination is 25 μg, but less than this amount of brucine can be detected by oscillopolarographic analysis especially in samples containing morphine, when the colour test with HNO_3 cannot be applied. W. J. BAKER

2301. **Separation and determination of ergot alkaloids by paper chromatography.** M. Pöhm (Pharmacognostic Inst., Vienna Univ.). *Arch. Pharm., Berlin*, 1958, **291** (9), 468–480.—The alkaloids were dissolved in a mixture of CCl_4, $CHCl_3$ and benzene or of CCl_4 and di-*n*-butyl ether, and separated by descending chromatography on Whatman No. 1 paper impregnated with formamide. For quant. determination, the individual zones were shaken with a mixture of tartaric acid and *p*-dimethylaminobenzaldehyde and the intensity of the blue coloration of the resulting soln. was measured photometrically. Secondary chromatograms were made of the zones containing unseparated alkaloids. In the case of ergometrine and ergometrinine, a mixture of benzene and pyridine was used as solvent. Zones containing ergocristine, ergocornine, ergocristinine and ergocorninine were chromatographed on a paper impregnated with dimethyl phthalate, with a mixture of formamide and water as solvent. M. H. SAWISTOWSKA

2302. **Assay of rauwolfia and its preparations.** W. C. Evans. *Pharm. J.*, 1958, **181**, 129–130.—Differences in the i.r. spectra of reserpine and reserpine containing 20% of deserpidine are described and illustrated; the u.v. spectra of the same samples were almost identical. N. E.

2303. **Two-dimensional separation of glycoalkaloids of the solanine complex by paper electrophoresis and chromatography and their colorimetric determination.** J. Šerák and M. Kutáček (Dept. of Chemistry, School of Agric., Prague). *Českosl. Farm.*, 1958, **7** (6), 322–324.—The glycoalkaloids (80 to 500 μg) were separated by paper electrophoresis on Whatman No. 1 paper in 2·5 *M* acetic acid at 140 V for 18 hr. A further chromatographic separation was performed in ethyl acetate - acetic acid - H_2O (11:1:2) in a direction at right angles to that of the original electrophoresis, and the spots were detected with $SbCl_3$ in $CHCl_3$. For a quant. determination, the spots were cut out, eluted with 1% acetic acid, and determined colorimetrically according to the method of Pfankuch (*Biochem. Z.*, 1937, **44**, 295) with slight modification. Partial losses of glycoalkaloids during the separation were observed (4 to 7%), and the use of a calibration curve is therefore recommended. J. VOLKE

2304. **Polarographic determination of xanthopurine alkaloids.** G. Dušinský and T. Čavaňák (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farm.*, 1958, **7** (9), 511–514.—Caffeine, theobromine and theophylline, although not reducible at the dropping-mercury electrode, may be determined polarographically after oxidation with Br. By evaluating the wave heights of the resulting substituted parabanic acids, even 0·24 mg of a xanthopurine alkaloid may be determined to within $\pm$ 3%. Barbiturates, acetylsalicylic acid, ephedrine, codeine, papaverine and digitoxin do not interfere, whereas amidopyrine, phenazone and phenacetin must be removed before the reaction

with Br. *Procedure*—Dissolve the sample in *N* acetic acid (hot for theobromine and theophylline) to a concn. of 25 to 100 mg per 100 ml. To this soln. (2 ml) add a satd. soln. of Br (1 ml) and make up the vol. to 10 ml with *N* acetic acid (immediately in the case of theophylline). Dissolved Br and O are removed in the polarographic vessel with a stream of N, and the polarographic wave is recorded and compared with that of a standard. J. VOLKE

2305. **Improved spectrophotometric method for determination of nicotine in tobacco smoke.** A. H. Laurene and T. G. Harrell (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1800–1802.—The method is a modification of that by Willits *et al.* (*Brit. Abstr. C*, 1950, 404), in which the u.v. absorption band of nicotine hydrochloride at 259 mμ is used. The acidic smoke concentrate is first steam-distilled to reduce the background spectrum. The recovery of added nicotine is ≃ 100%, and results are in good agreement with values obtained by the gravimetric tungstosilicate method. Duplicate determinations generally agree to within 2%. G. P. COOK

2306. **Identification of carcinogenic hydrocarbons in tobacco smoke.** A. Pietzsch (Chem. Lab. des Stadtkrankenhauses, Dresden-Friedrichstadt). *Naturwissenschaften*, 1958, **45** (18), 445.—A neutral condensate of tobacco smoke is produced from machine-smoked cigarettes. Care is taken to assure that the temperature of the glowing point is the same as that of naturally smoked cigarettes, *i.e.*, 720° to 740°. "Background absorption" is reduced by removal of unsaturated hydrocarbons, esters and ketones by repeated chromatography on activated alumina and suitable chemical purification. Spectrographic examination then reveals the following main polycyclic hydrocarbons (5 groups in order of magnitude)—(*i*) anthracene, fluorene, 1:2-benzanthracene, 1:2-5:6-dibenzanthracene; (*ii*) perylene; (*iii*) fluoranthene, 9:10-dimethyl-1:2-benzanthracene, 1:2-benzopyrene; (*iv*) chrysene, pyrene; and (*v*) phenanthrene and 3:4-benzopyrene. The quant. relationship between these 5 groups is as 2:3:4:5:6. It is confirmed that the amount of 3:4-benzopyrene depends to a large extent on the method of extraction and elution. The solvents must not be purified with the aid of conc. H_2SO_4. E. KAWERAU

2307. **Determination of calcium in tobacco—complexometric evaluation with EDTA.** A. Ollero Gómez and V. Cortés Muñoz. *Bol. Inst. Nac. Invest. Agron., Madrid*, 1958, **18** (38), 271–293.—Tobacco is ashed by the A.O.A.C. method and the ash from 2 g is dissolved and the Ca determined with EDTA in the usual way, with murexide as indicator. The interfering effects of PO_4^{3-}, Mg^{2+} and Fe^{3+} are shown to be small for normal tobacco. L. G. L. UNSTEAD-JOSS

2308. ***Hypericum perforatum* L. I. Qualitative investigation of the individual parts of the plant in blossom.** M. Kučera (Res. Inst. for Medicinal Herbs, Prague). *Českosl. Farm.*, 1958, **7** (7), 391–393.—Hypericin ($R_F = 0{\cdot}9$), rutin ($R_F = 0{\cdot}5$) and quercetin ($R_F = 0{\cdot}7$) are most easily separated in a system containing *n*-butanol - acetic acid - H_2O (4:1:5) on S. & S. paper 2043b. Chlorophyll does not interfere. Hypericin and rutin are present in all parts of the plant, whereas quercetin is in decaying red leaves only.

II. The use of partition paper chromatography for the determination of hypericin and rutin in Herba hyperici. M. Kučera. *Ibid.*, 1958, **7** (8), 436–438.—The coarsely powdered sample is extracted with $CHCl_3$ for 1 hr. for removal of chlorophyll, after which an extraction with methanol - pyridine follows. The extract is analysed by chromatography (*n*-butanol - acetic acid - H_2O) (4:1:5). The spots of hypericin (**I**) ($R_F = \simeq 0{\cdot}9$) and rutin (**II**) ($R_F = 0{\cdot}5$) are detected in u.v. light. **I** is extracted from the spot with methanol - pyridine, and the extinction of the pink soln. is determined directly with a green filter. **II** is extracted with 0·1 *N* HCl and determined after coupling with diazotised sulphanilic acid. J. VOLKE

2309. **Determination of the proteolytic activity of pharmaceutical preparations.** H. Nidecker (Kontroll- und Betriebslab. der Dr. A. Wander A.-G., Bern). *Pharm. Acta Helv.*, 1958, **33** (8–9–10), 559–570 (in German).—Various methods of determination are reviewed (66 references). The nephelometric method of Gross and the spectrophotometric method of Kunitz (*J. Gen. Physiol.*, 1947, **30**, 291) are recommended. The results of titrimetric assays give a less accurate picture of the protein degradation. A. R. ROGERS

2310. **Estimation of the activity of cellulases intended for use in therapy.** H. Desarménien and C. Bastien (Lab. Wander, Champigny-sur-Marne, Seine, France). *Pharm. Acta Helv.*, 1958, **33** (8–9–10), 583–601 (in French).—Cellulase activity may be determined by measurement of the rate of decrease of viscosity of a methylcellulose soln., the rate of liberation of reducing sugars from methylcellulose, or the rate of dissolution of Cellophane. The relative merits of these methods are compared. A. R. ROGERS

2311. **Microbiological assay of antibiotics in the Pharmacopoeia Helvetica.** M. Vuilleumier and L. Anker (Eidg. Pharmakopöelab., Bern). *Pharm. Acta Helv.*, 1958, **33** (8–9–10), 621–633 (in German).—An agar-diffusion method is described for the microbiological assay of bacitracin, chlortetracycline, neomycin, oxytetracycline and tyrothricin. A number of different strains of *Sarcina lutea* may be used. Turbidimetric methods of determination of tyrothricin are regarded as unsuitable for inclusion in the pharmacopoeia. A. R. ROGERS

2312. **Determination of the relative proportions of tetracycline and chlortetracycline in culture fluids.** I. I. Belousova and L. A. Popova (Antibiotics Res. Inst., Moscow). *Antibiotiki*, 1958, **3** (6), 24–26.—The culture fluid of *Actinomyces aureofaciens* was used. The tetracycline antibiotics which formed during fermentation were separated by paper chromatography and then determined colorimetrically. The solvent used was *n*-butanol - acetic acid - water (2:1:1). The filter-paper was steeped in a phosphate buffer (0·3 *M*) at pH 2·53. After 6 to 8 hr. the air-dried chromatograms were irradiated by u.v. light and the antibiotics were revealed as yellow - orange spots. Portions of the spotted filter-papers were treated with 2 *N* HCl (5 ml) for 5 min. in a boiling-water bath. The hydrolysates were determined photometrically and the antibiotic concn. calculated by reference to standard curves. K. R. C.

2313. **Therapeutically used esters of nitric acid and methods for their quantitative determination.** P. Frauch and A. Bürgin (Pharm. Inst., Univ. Bern) *Pharm. Acta Helv.*, 1958, **33** (8–9–10), 527–546 (in

German).—The physical properties of these nitrates are briefly reviewed. A number of methods of assay are examined, with special reference to their accuracy and reproducibility and to the effect of interfering substances such as pharmaceutical excipients. Potentiometric redox titration with Fe^{3+} is preferred for the assay of the pure substances, and extraction of the active principle followed by colorimetric determination with phenoldisulphonic acid for pharmaceutical preparations. The accuracy is $\simeq \pm 1\%$. A method of reduction to the alcohol and oxidative determination of the alcohol with periodic acid is less accurate, but is of some value. Procedures based on alkaline saponification or on hydrolysis or reduction followed by ammonia distillation are in general not recommended.

A. R. Rogers

2314. **Detection reactions of barbiturates.** V. Jokl and E. Janečková (Dept. of Anal. Chem., School of Pharmacy, Brno, Czechoslovakia). *Českosl. Farm.*, 1958, **7** (7), 397–398.—A selective reaction for barbiturates and hydantoins based on Zwikker's reaction is suggested. The chromatogram is treated with a soln. of $[Cu(pyridine)]^{2+}$ and then with 0·001 *M* EDTA (disodium salt). The spots are detected by immersion in a 0·25% soln. of Na diethyldithiocarbamate. After a chromatographic separation 10 μg may be detected, and 5 μg in a spot test. Uracil and thiobarbiturates react in the same way; 1-alkyl derivatives do not react because of their inability to form an enolic group in the 2-position.

J. Volke

2315. **Detection of barbiturates on paper chromatograms by addition of chlorine to their amide group.** G. Rentsch (Strasse der Jugend 28, Magdeburg, Germany). *Naturwissenschaften*, 1958, **45** (13), 314.—The solvent system recommended is pyridine - water - aq. NH_3 (7:3:1) in a descending run on paper that has been impregnated with *M* KNO_3. The method for detecting the barbiturate by addition of chlorine is that described by Zahn and Rexroth (*Anal. Abstr.*, 1956, **3**, 1055).

E. Kawerau

2316. **Nephelometric determination of phenobarbitone.** K. Kalinowski and H. Baran (Inst. of Pharmaceutical Chem., Acad. Med., Lodz, Poland). *Acta Polon. Pharm.*, 1958, **15** (5), 327–331.—Mercuric perchlorate is used as the reagent for the determination of phenobarbitone in the Pulfrich nephelometer. The relative and absolute turbidities of the soln. and their relation to the concn. of phenobarbitone are determined. The method enables 0·1 mg to 0·35 mg of phenobarbitone to be determined. The error does not exceed $\pm 4\%$. The time of one determination is 5 min.

H. Dmowska

2317. **Determination of barbiturate after putrefaction.** E. J. Algeri (Harvard Univ., U.S.A.). *J. Forensic Sci.*, 1957, **2**, 443–455.—Samples of human liver, obtained at autopsy, from an individual who had succumbed to barbiturate intoxication were (*a*) stored without attempts at preservation; (*b*) immersed in formaldehyde soln.; (*c*) immersed in embalming fluid. These experiments were all performed at 27°. At periodic intervals, aliquots of the unpreserved tissues were analysed spectrophotometrically. Subsequently the soln. used in the u.v. spectrophotometric determination of apparent barbiturate was re-extracted into ether, the ether evaporated, and the residue submitted to an ascending paper-chromatographic analysis. The real barbiturate thus isolated was then assayed. Up to 12 days after exposure at room temp., the barbiturate was easily detected by both techniques, with a 50% increase in the apparent barbiturate concn. Thereafter the u.v. analysis before chromatography was unsatisfactory, but the eluted material from the paper chromatogram gave the same 50% increase up to 90 days after the original date. The preserved tissues, as well as the surrounding embalming fluids and formaldehyde, were also analysed periodically. Up to 5·5 months after their initial immersion, barbiturates were detectable in both the tissues and the fluids.

Chem. Abstr.

2318. **Quantitative determination of piperazine in pharmaceutical preparations.** M. Hädicke (Staatl. Inst. für Arzneimittelprüfung, Jena). *Pharm. Zentralh.*, 1958, **97** (8), 365–367.—Piperazine hydrate may be determined by pptn. of the tetraphenylboron salt, followed by argentimetric titration (*cf.* Rüdorff and Zannier, *Brit. Abstr. C*, 1953, 50), or by pptn. of the reineckate, followed by hydrolysis and Volhard titration (*cf.* Vogt, *Pharm. Zentralh.*, 1951, **90**, 1). Both methods are accurate to approx. $99 \pm 0{\cdot}5\%$. The methods have been successfully applied to the assay of a syrupy preparation of piperazine.

A. R. Rogers

2319. **A new volumetric method of determination of phenothiazine compounds.** G. Dušinský (Food Res. Inst., Bratislava). *Pharmazie*, 1958, **13** (8), 478–480.—The method is an oxidative titration and is applied to promethazine, diethazine, chlorpromazine and prochlorperazine. The titrating agent is ceric sulphate or KBr - $KBrO_3$ in acid soln. The end-point is determined by a dead-stop method. The red colour and the current intensity reach a max. when 1 equiv. of the titrant has been added. Thereafter the colour and the current intensity diminish until they reach a minimum when 2 equiv. have been added.

N. E.

2320. **Use of Wofatit F for the quantitative evaluation of reineckate precipitations: determination of Rodipal, Thiantan and Propaphenin [chlorpromazine].** K. Howorka (Staatl. Inst. für Arzneimittelprüfung, Jena). *Pharm. Zentralh.*, 1958, **97** (8), 374–377.—In this determination of thiocyanate in insol. reineckates, the ppt. is hydrolysed and the thiocyanate soln. is converted, by passage through the H^+ form of the cation-exchange resin Wofatit F, into free thiocyanic acid, which is titrated with alkali. The method is applied to the determination of phenothiazine derivatives which interfere with the determination by the argentimetric method of Vogt (*cf. Pharm. Zentralh.*, 1951, **90**, 1). A U-tube form of column is described which allows the liquid to flow upwards through the resin and so avoids clogging by pptd. $Cr(OH)_3$.

A. R. Rogers

2321. **Determination of nicotinaldehyde thiosemicarbazone.** B. Buděšínský and J. Vachek (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1958, **7** (5), 241–245.—Several methods are proposed for the determination of nicotinaldehyde thiosemicarbazone (**I**). The compound (10 to 50 mg) may be titrated in 5 *N* NaOH potentiometrically with 0·1 *N* iodine. When **I** (30 to 70 mg in 30 ml of H_2O) is heated for 10 min. with $Cd(OH)_2$ [Cd acetate (5 ml) and *N* NaOH (5 ml)], CdS is formed. This is filtered off and washed, and treated

with 0·1 *N* iodine (10 ml), conc. HCl (3 ml) and H_2O (30 ml). The excess of iodine is titrated with $Na_2S_2O_3$ soln. In a polarographic method the anodic waves corresponding to the reaction of R·S⁻ with Hg ions are used. J. VOLKE

2322. **Coulometric determination of Nipagin A [ethyl 4-hydroxybenzoate] and phenyl salicylate by the use of cuprous salts and bromides as the dual intermediates.** K. Kalinowski and A. Piotrowska (Inst. Pharm. Chem., Acad. Med., Lodz, Poland). *Acta Polon. Pharm.*, 1958, **15** (5), 321–325.—Micro-determination of ethyl 4-hydroxybenzoate and phenyl salicylate is carried out by bromination with bromine obtained from electrolysis. The excess of bromine is measured coulometrically using platinum electrodes and cuprous salts and bromide. Results obtained by this method differ by ± 0·5% from the mean of the results obtained by the macro-method. H. DMOWSKA

2323. **Chelatometric titrations in pharmaceutical analysis. XVIII. Determination of bismuth in mixtures.** V. Suk, O. Koldinský and M. Malát (Dept. of Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1958, **7** (5), 249–251.—A chelatometric titration of bismuth with catechol violet as indicator has been used for the specific determination of Bi in pharmaceuticals. J. VOLKE

2324. **Complexometric determination of magnesium in some prescription mixtures.** J. Terpiłowski and K. Szmyt (Inst. of Inorg. and Anal. Chem., Acad. Med., Wrocław, Poland). *Acta Polon. Pharm.*, 1958, **15** (4), 285–292.—The concn. of Mg is determined by titration with EDTA (disodium salt) at pH 10, using an aq. NH_3 - NH_4Cl buffer and Eriochrome black T as indicator. The interfering substances present in the prescription mixture are removed by passing the soln. under test through a column of anionite Amberlite IRA-400. Bismuth salts are removed by hydrolysis. Satisfactory and quick results are obtained. H. DMOWSKA

See also Abstracts—**2222**, Determination of salicylic acid in acetylsalicylic acid. **2240**, Determination of carvone in caraway oil. **2259**, Determination of phenazone in serum. **2270**, Determination of adrenaline and noradrenaline. **2276**, Assay of dimercaprol. **2342**, Determination of sugars in malt extract.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

2325. **Limits of accuracy in the polarimetry of raw sugar.** W. Schiebel. *Zucker*, 1958, **11**, 182–187.—Possible sources of error in the method and means for obviating them are discussed in detail, with special consideration of possible absorption of moisture during sampling and weighing of the sugar, the use of accurately calibrated measuring flasks (error ≯ 0·02 g in weight of contents) with necks of 10-mm diameter, the removal of foam by blowing ether vapour over the top, the lead error in clarification, and the accuracy of the polarimeter, temp. control and the light source.

SUGAR IND. ABSTR.

2326. **Refined test techniques for polarising raw sugar.** E. J. Culp and H. E. Sommer. Amer. Chem. Soc., 134th Meeting, September 1958, Abstr. of Papers, p. 21D.—The effects of three procedures on the polarimetry of raw sugars were studied. The average pol of sugar samples measured at a controlled temp. of 20° and a r.h. of 50% was 0·03° *S* lower than when the pol was measured under uncontrolled conditions which do not minimise loss of moisture (35°, 35% r.h.). When sugar samples were defecated and then mixed with water to give a total vol. of 90 ml, an increase of 30 ml compared with the conventional method, the pol was calculated as being 0·06° *S* lower. Ordinary raw-sugar flasks were found to contain an average of < 100 ml. Selection of flasks to conform to the limits 100 ± 0·01 ml has given an estimated decrease of pol readings of 0·03° *S*.

SUGAR IND. ABSTR.

2327. **The chromatographic determination of dextrose and laevulose in raw sugars, molasses and other sugar products.** F. J. Gardiner and E. G. Muller (Tate & Lyle Res. Lab., Keston, Kent, England). *Int. Sugar J.*, 1958, **60**, 256–258.—The procedure, drying oven and viewing-box employed are those of Albon and Gross (*Analyst*, 1952, **77**, 406, 410). Dilute the sample so that the soln. contains 0·04 to 0·60% of glucose + fructose. Apply aliquots (5 μl) to Whatman No. 1 paper, together with a series of standards of glucose + fructose covering the above range of concn. The standards contain sucrose and KCl in amounts equivalent to the sucrose and ash in the diluted sample, and papers are prepared in duplicate, one being used for glucose, the other for fructose. Develop with *n*-propanol - water - ethyl acetate (7:2:1) for 40 hr. at 15° to 20° and dry in the oven. Spray the fructose paper with 2% 1-naphthol in 50% industrial alcohol, to which 10% of orthophosphoric acid is added immediately before spraying. Heat at 85° to 90° for 10 min. and place at once between glass plates to prevent fading. Ketose sugars give blue spots on a white ground. Spray the glucose paper with 0·5% *p*-aminodiethylaniline sulphite in 50% industrial alcohol containing 2·5% of phthalic acid, and dry for 4 min. at 115° to 120°. Aldose sugars give brown or reddish-brown spots on a white ground. The sample spots are read by visual comparison with the standard spots in the viewing-box. Although the chromatography takes 40 hr., the actual working time is small, and results are obtained rapidly after spraying. Results for glucose and fructose are not interfered with by other sugars, and the precision is ± 10%. Results are quoted for raw cane sugars and cane molasses and compared with those by the method of Lane and Eynon. R. E. ESSERY

2328. **Determination of calcium in sugar-house products with ethylenediaminetetra-acetic acid (EDTA).** N. A. Ramaiah, Vishnu and R. K. Chaturvedi (Dept. Phys. Chem., Nat. Sugar Inst., Kanpur, India). *Naturwissenschaften*, 1958, **45** (12), 290–291 (in English).—Diluted and clarified molasses is used. Excess of lead and interfering ferric salts are removed with $K_4Fe(CN)_6$. A few drops of conc. HNO_3 are added and a measured volume of the solution is then added to ammoniacal copper sulphate and titrated with EDTA (disodium salt) soln., noting the colour change at 630 mμ spectrophotometrically. Alternatively, titration, with murexide as indicator, can be used.

E. KAWERAU

2329. **Simultaneous determination of iron and copper in milk and milk products.** R. Alifax and M. Bejambes (Stat. Centrale Microbiol. Recherches Laitières, Jouy-en-Josas, France). *Lait*, 1958, **38**, 146–160.—The method of Ventura and White (*cf. Anal. Abstr.*, 1954, **1**, 759) for determining Fe and Cu in serum was adapted for milk and milk products. The material is prepared by the action of HNO_3, $HClO_4$ and H_2SO_4, fat being extracted from cream and butter by benzene. Iron is determined by formation of a complex with 2:2′-dipyridyl, and Cu as diethyldithiocarbamate at pH 4·4, at which the colours of the two compounds do not interfere with each other. The method is rapid and allows a rapid selection of butters for preservation, eliminating those in which the Fe and Cu contents are too high for prolonged storage.
NUTR. ABSTR. REV.

2330. **Determination of manganese in milk.** W. B. Healy (Soil Bureau, D.S.I.R., Box 8001, Wellington, New Zealand). *J. Agric. Food Chem.*, 1958, **6** (8), 606–608.—Manganese is determined by the periodate method in 100-ml samples of milk, after removing Ca as phosphate in the presence of trisodium N-hydroxyethylethylenediaminetriacetate, which retains Mn. The permanganate extinction is measured in 5-cm cells which require only 6 ml of soln.
M. D. ANDERSON

2331. **Paper electrophoresis of the proteins of whey obtained from milk and powdered milk. II.** H. Frehse and H. Fink (Inst. f. Gärungswiss. u. Enzymchem., Univ. Köln, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (9), 811–817.—Samples of whey obtained from fresh milk and from reconstituted dried milk of both the cylinder-dried and spray-dried variety revealed different and characteristic patterns of protein composition, lactoglobulin and lactalbumin being the predominant fractions. The technique is described in detail.
A. TESSLER

2332. **Modified Teichert [determination of] fat in cheese.** W. V. Falkenhahn (Dairy Div., Dept. of Agric., Auckland, N.Z.). *Indian J. Dairy Sci.*, 1958, **11** (2), 76–79.—In view of the disadvantages of the usual van Gulik method when used for routine determinations of fat in cheese, the Teichert method for fat in dried milk was modified for the purpose. Grated samples are weighed in tared aluminium boats and transferred to 70% Teichert dried-milk butyrometers via wide-mouthed glass funnels. Serial pipetting units and electric rotatory shakers can be used. High fat readings because of excessive formation of amyl ester and ether are eliminated by using H_2SO_4 of sp. gr. 1·820, with consequent sudden rise of temp. to 81° at the beginning of the digestion, which is continued at 65° to 68°. Results on Cheddar cheese agreed well with those of the gravimetric British Standard method. Special 50% Teichert cheese butyrometers (0·05% subdivided) are suggested for this test.
M. D. ANDERSON

2333. **Separation of vanillin, ethylvanillin and their isomers by paper chromatography.** F. Vonášek (Aroma n.p., Prague). *Průmysl Potravin*, 1958, **9** (6), 315–316.—A mixture of vanillin, *iso*vanillin, dialdehyde (4-hydroxy-5-methoxy*iso*phthalaldehyde), *iso*ethylvanillin, ethylvanillin, veratraldehyde, 5-ethoxy-4-hydroxy*iso*phthalaldehyde, *o*-vanillin, *o*-ethylvanillin, 3:4-diethoxy- and 2:3-diethoxy-benzaldehyde can be separated by chromatography in $CHCl_3$ soln. on Whatman No. 4 paper impregnated with 20% formamide or dimethylformamide soln. in ethyl acetate, developing with light petroleum - benzene (2:1). The spots are detected first with $FeCl_3$ soln. (2% in 1% HCl), then with 2:4-dinitrophenylhydrazine soln. (0·4% in 2 *N* HCl). The spots can be eluted and the colours measured.
J. ZÝKA

2334. **Contribution to the chemistry and analysis of alginic acid. II.** W. Diemair and H. H. Weichel (Inst. Lebensmittelchemie, Univ., Frankfurt). *Dtsch. Lebensmitt. Rdsch.*, 1958, **54** (7), 151–155.—Available methods for the detection of alginates and other thickening agents are reviewed and tabulated. Alginates are characterised by forming ppt. with both 10% $CaCl_2$ soln. and Zwikker's reagent (1 ml of pyridine + 10 ml of 5% $CuSO_4$ soln.), or by detection by paper chromatography of D-mannose in the hydrolysate. Colour reactions for alginates are unreliable. For detection in milk, chocolate drinks or ice-cream, boil 30 g for 30 sec. with 50 ml of 5 *N* HCl and a little sand, cool, add 30 ml of 96% ethanol and centrifuge. Wash the residue with ethanol, then with ether and air-dry. Dissolve in 0·1 *N* NaOH (10 ml), and re-precipitate with ethanol. Repeat the dissolution and pptn. until the ppt. is colourless, and apply pptn. tests to the alkaline soln. For mayonnaise or thickened soups, dry 10 g to 50 g with sand, extract (Soxhlet) with CCl_4 or trichloroethylene, warm the fat-free residue with 0·1 *N* NaOH (20 ml), filter, evaporate to about 5 ml and test. The limits of detection are about 0·02% for milk and 0·2% for mayonnaise.
E. C. APLING

2335. **Paper-chromatographic identification of preservatives in food.** H. Cats and H. Onrust (Keuringsdienst van Waren, Rotterdam). *Chem. Weekbl.*, 1958, **54** (35), 456–459.—Extract the sample with ether (2 × 25 ml), shake the extract with 10 ml of 4 *N* NaOH and acidify the aq. layer with 4 *N* H_2SO_4. Extract with ether (2 × 10 ml), dry the ether layer with Na_2SO_4 and evaporate to 1 ml. Prepare a chromatogram of 50 µl on S. & S. paper 2043b Mgl with *n*-butanol - aq. NH_3 - H_2O (7:2:1); spray with quinine soln. (1% in ethanol), dry at 25° and observe the fluorescent spots in u.v. light (366 mµ). Spray with diazotised sulphanilic acid in 0·5 *N* Na_2CO_3. R_F values of benzoic acid, salicylic acid, *p*-hydroxybenzoic acid and its esters, *p*-chlorobenzoic acid, sorbic acid, dehydracetic acid, propionic acid, formic acid, glycollic acid, iodoacetic acid, bromoacetic acid and chloroacetic acid are given.
P. RENTENAAR

2336. **Determination of sulphurous acid in foods.** J. F. Reith and J. J. L. Willems (Abt. Lebensmittelchem., Univ., Utrecht, Holland). *Z. Lebensmitt-Untersuch.*, 1958, **108** (3), 270–280.—The apparatus described comprises a boiling-flask, with inlets for CO_2 and for the introduction of the sample, connected through a reflux condenser with an absorption vessel containing 3% H_2O_2. The SO_2 is liberated by boiling the sample with dil. HCl for 1 hr. in a current of CO_2. The H_2SO_4 formed in the receiver is determined alkalimetrically or by the addition of a known excess of $BaCl_2$, followed by boiling and complexometric titration to determine the amount of Ba pptd. as $BaSO_4$. The results are not affected by the presence of volatile acids, H_2S, amino acids containing S, mustard oil, < 5 mg of Cu, or < 25 mg of acetaldehyde. Mustard and onions yield negligible amounts of SO_2. Dried and fresh egg-albumin yield ≃ 70 and ≃ 25 mg of SO_2

per kg of dry matter, respectively. Added SO_2 (as sulphite equiv. to 1 to 55 mg) is generally recovered in 95 to 100% yield, but low results (by 25 to 50%) are unaccountably obtained for additions to tomato products, chocolate paste, and dried plums or figs. The results of alkalimetric and complexometric determinations agree well except for determinations made on egg-albumin or onions. Data for the SO_2 content of a number of foods are considered from the point of view of public health. P. S. ARUP

2337. **Determination of dehydracetic acid.** M. Kukal-Belohlavy and L. Schmid (II Chem. Univ., Vienna). *Z. LebensmittUntersuch.*, 1958, **108** (3), 238–244.—The literature dealing with the preservative properties of dehydracetic acid (**I**) is reviewed. The **I** is extracted from foods by ether or dichloroethane, and then extracted into 0·1 *N* NaOH (two portions of 1·5 to 2 ml each). The method depends on the measurement of the amount of iodine absorbed by the **I** in the formation of iodoform. *Procedure*—To 1 ml of the alkaline extract (contained in a flask provided with a glass stopper) add *N* NaOH (7·5 ml) and 0·01 *N* iodine (5 ml), and set aside overnight at 4°. Acidify the soln. and back-titrate with 0·005 *N* thiosulphate. The iodine soln. (ml) consumed × 0·1326 gives the content of **I** (mg). A blank test is simultaneously carried out with 1 ml of water. The method allows of the determination of 0·1 to 0·7 mg of **I**. The recovery of **I** from foods varies from 97·7 to 101·5%. A qual. test can be made by adding to 1 ml of the alkaline extract 25% NaOH (1 ml) and 0·1 *N* iodine (1 ml); a distinct turbidity formed after 5 to 15 min. indicates the presence of ⩽ 0·01 mg of **I**. P. S. ARUP

2338. **Colorimetric methods for the determination of sorbic acid.** H. J. Hardon and D. Visser (Keuringsdienst van Waren, Amsterdam, Holland). *Z. LebensmittUntersuch.*, 1958, **108** (5), 397–402.—To avoid the occurrence of excessive blank values, the Melnick and Luckman steam-distillation process (*Food Res.*, 1955, **20**, 649) for the separation of sorbic acid from foods should be conducted with a constant vol. of still-liquor at temp. ⩾ 105°. Blank values can further be reduced to negligible proportions by making the distillate alkaline and evaporating it to 25% of its bulk. For the colorimetric determination, the sorbic acid is quant. extracted from the conc. acidified distillate by dichloromethane; after drying with Na_2SO_4, an aliquot portion of the extract (8 ml out of 100 ml) is mixed in a glass-stoppered test-tube with Wijs soln. (2 ml). After a reaction time of 15 min. in darkness, the liberated iodine is measured colorimetrically at 520 mμ. For the range 0 to 30 mg of sorbic acid per 100 ml of extract, the relationship is linear. The recovery of sorbic acid (> 90%) is equiv. to that obtained by direct spectrophotometric measurement at 260 mμ made on the distillate. Sorbic acid also gives a colour reaction (green) on heating at 130° with H_2SO_4 and quinol, and extraction of the mixture (previously made alkaline) with benzene; this reaction is suitable for identification.

P. S. ARUP

2339. **Determination of sorbic acid in foods.** P. Spanyár and A. Sandor (Forschungsinst. f. Konserven-, Fleisch- u. Kälteindustrie, Budapest, Hungary). *Z. LebensmittUntersuch.*, 1958, **108** (5), 402–405.—Sorbic acid can be determined in acid aq. soln. by measurement of the amount of bromine (added as 0·02 *N* $KBrO_3$) absorbed in 15 min. in darkness; the technique is similar to that used in the determination of the iodine or bromine values of fats. Salicylic acid, if present, must be determined separately, and allowance made for the Br which it absorbs. In preparation for the determination, the acid is extracted by ether from fruit juices or aq. extracts of fruit or vegetables in the presence of H_2O_2, which is added to destroy reducing substances which interfere with the determination; separation from dairy products or fats is achieved by the Melnick and Luckman distillation process (*Food Res.*, 1955, **20**, 649). The range of the method is 2 to 10 mg of sorbic acid, corresponding to 5 to 10 g of the sample. The probable error is ± 2·2%, and the maximum error ± 5%. P. S. ARUP

2340. **A proof of adulteration of coffee with coffee substitutes by the use of paper chromatography.** B. Škárka and Z. Raděj (Control Inst. of Food Industry, Bratislava). *Prúmysl Potravin*, 1958, **9** (8), 413–415.—*Procedure*—Extract the sample (1 g) for 1 hr. with hot H_2O (10 ml), filter and evaporate to 2 ml. Place 25 μl of this soln. on the chromatographic paper (diam. 27 cm) and develop with butanol - acetic acid - H_2O (4:1:5) as the solvent system. Dry and detect the spots of adulterant (chicory) by means of aniline phthalate as reagent (pink colour which changes to yellow at 105°). Another procedure consists in hydrolysis of the sample with *N* H_2SO_4 in a sealed test-tube and in two-step chromatography with (*a*) butanol - pyridine - H_2O (10:3:3) and (*b*) butanol - acetic acid - H_2O (4:1:5). The presence of xylose and mannose, which can be the constituents of adulterants, can be detected with aniline phthalate as in the previous case. J. ZÝKA

2341. **Technique for the determination of rapidly reducing substances in wort and beer.** H. Schilfarth and K. Apel (Versuchs- und Lehranstalt für Brauerei, Berlin, Germany). *Brauerei, Wissen. Beil.*, 1958, **11** (9), 121–127.—A portion of bottled beer is first freed from CO_2 under reduced pressure with the use of decyl alcohol (3 ml) as an anti-foaming agent. The method consists in allowing an excess of 0·001 *N* dichlorophenolindophenol (**I**) (usually 1·5 ml) to act on the sample (15 ml), buffered at pH 4·2, for 18 sec. at 20°; the unconsumed **I** is then extracted from the aqueous phase with ether (33·5 ml) and determined in the ethereal soln. by colorimetric measurement at 530 mμ in comparison with the results of blank tests conducted with water and known amounts of 0·001 *N* **I**. To avoid atmospheric oxidation a special apparatus is used. The reducing value (R) is calculated from the following formula, which corrects for the variation in R with the amount of **I** in excess: $(Z - 1{\cdot}5\ W)F$, where Z = vol. (ml) of 0·001 *N* **I** employed, W = vol. (ml) of 0·001 *N* **I** unconsumed, and F is a factor = 200 for 5 ml, and 66·7 for 15 ml of the sample. The reproducibility of the method is satisfactory. P. S. ARUP

2342. **Paper-chromatographic examination of sugars in malt extract.** J. Büchi and R. Gräub (Pharm. Inst., E. T. H., Zürich). *Pharm. Acta Helv.*, 1958, **33** (8–9–10), 547–558 (in German).—Aqueous dilutions of malt, wort and extract of malt were submitted to chromatography on Whatman No. 1 paper with *n*-butanol - acetic acid - H_2O (4:1:5) as descending solvent for ≃ 70 hr. The separated reducing sugars were determined by elution with hot water and colorimetry with Somogyi - Nelson reagent. A. R. ROGERS

2343. **Occurrence and formation of amines in beer, wort, malt and barley.** B. Drews, F. Just and H. Drews (Inst. für Gärungsgewerbe, Berlin, Germany). *Brauerei, Wissen. Beil.*, 1958, **11** (9), 169–180.—To separate the volatile amines, the beer or wort, made alkaline with Na_2CO_3, is vacuum-distilled into a receiver containing N H_2SO_4. The acid distillate is evaporated to dryness *in vacuo*. After removal of NH_4^+ from a soln. of the residue by pptn. as sodium ammonium cobaltinitrite, methylamine, dimethylamine, propylamine, *iso*butylamine and *iso*amylamine are separated and determined chromatographically with *n*-butanol - acetic acid - water (4:1:1) as ascending solvent. Methylamine can be determined separately by the method of Gove *et al.* (*cf. Anal. Chem.*, 1951, **23**, 721), and dimethylamine as Cu dimethyldithiocarbamate. The non-volatile amines hordenine and tyramine are separated from the alkaline still-residue by extraction with amyl alcohol, and determined by chromatographic analysis. Choline is determined by a microbiological method. Beer (excluding special beers) contains 19 to 31 mg of NH_4^+ per litre. The content of aliphatic amines ranges from $\simeq$ 0·36 μg (for methylamine) to $\simeq$ 0·83 μg per litre for *iso*amylamine. Contents of hordenine, choline and tyramine are 3 to 6 mg per litre, 200 to 340 mg per litre, and slight traces, respectively.

P. S. Arup

2344. **Determination of lactic acid and volatile acids in "Berlin white beer" and their significance in the calculation of original wort.** K. Silbereisen and C. Kremkow (Versuchs - und Lehranstalt für Brauerei, Berlin). *Brauerei, Wissen. Beil.*, 1958, **11** (9), 128–133.—The volatile acids are separated from the CO_2-free beer by steam-distillation and determined by titration. The still residue, containing the lactic acid, is first freed from proteins by pptn. with acidified aq. sodium metaphosphate, and from sugars by pptn. with aq. $CuSO_4$ and a suspension of $Ca(OH)_2$. The lactic acid is determined in an aliquot of the final filtrate by oxidation to acetaldehyde with $KMnO_4$ in a Lieb - Zacherl distillation apparatus as described by Paul (*Anal. Abstr.*, 1954, **1**, 3118), the aldehyde being determined as bisulphite by iodimetric titration. For the determination of original wort in bottle-fermented beers, an additive correction is applied to the Balling value, which is based on the relationship of the volatile acid content (as acetic acid) to the sp. gr. of the beer. For beers made by open top-fermentation, the Schild and Schneider formula (*cf. Brauwissenschaft*, 1957, 298) is preferable.

P. S. Arup

2345. **Rapid determination of α-acids and moisture content of green hops.** L. Isebaert (Hogere Tech. Browerijskoll, St. Lieveen, Ghent, Belgium). *Brauwelt, B*, 1958, **98** (37), 663–665.—A slightly modified form of the method of Hartong *et al.* has proved useful for ascertaining the most favourable time for hop-picking with respect to the bittering value of the hops. An extract of the sample (30 g fresh or 15 g dry) is titrated conductimetrically with a 1% (instead of 4%) soln. of Pb acetate. Moisture is determined by i.r. drying.

P. S. Arup

2346. **Spectrophotometric analysis of wine spirit.** M. J. De Vries (Stellenbosch-Elsenburgse Landboukollege, Stellenbosch). *S. Afr. J. Agric. Sci.*, 1958, **1** (2), 195–202.—The rapid and reliable method described for determining the quality of alcohol distilled from wine is based on measurement of absorption at 218 mμ; this is an indication of the content of secondary constituents. Correlations of absorption with organoleptic rating and with fusel-oil content were good.

M. D. Anderson

2347. **Determination of fraud by addition of sucrose to musts and wines.** S. Dussaillant Bonitez (Univ. de Chile, Fac. de Agron.). *Bol. Inst. Nac. Invest. Agron., Madrid*, 1958, **18**, 85–236.—A wine sample is considered genuine, doubtful or fraudulent when the results of the following determinations lie within the limits quoted—ash $>$ 2 g per litre; 1·5 to 2 g per litre; $<$ 1·5 g per litre; alkalinity of ash, $>$ 17 milli-equiv. of NaOH per g; 15 to 17 milli-equiv. of NaOH per g; $<$ 15 milli-equiv. of NaOH per g; pH of complete neutralisation of the total acidity, 7 to 8; 8 to 8·6; $>$ 8·6; the pK of the wine, $<$ 5·0; 5·0 to 6·0; $>$ 6·0. Dry extract should be $>$ 15 g per litre. A summary of wine analysis is presented with 98 references.

L. G. L. Unstead-Joss

2348. **New method of determination of tartaric acid in wine.** I. Mareca Cortés and C. Diez de Bethencourt (Dept. Ind. Ferment., C.S.I.C., Madrid). *Ind. Aliment. Agric.*, 1958, **75** (7–8), 563–566.—The wine (10 ml) is decolorised with activated carbon (0·3 g). The carbon is treated in a current of steam for 3 hr., and the condensate is concentrated to $\simeq$ 10 ml and added to the filtrate. After acidifying with a few drops of HCl, ethanol satd. with Ba tartrate (80 ml) is added and after standing for 4 hr. the pectins are filtered off and washed with 20 ml of ethanol. The filtrate is neutralised with N NaOH to phenolphthalein, $BaCl_2$ soln. (5 ml) is added and after 3 to 4 hr. at 0° the ppt. is washed with ethanol satd. with $BaCl_2$ and then with abs. ethanol. The ppt. is dissolved in hot water, N H_2SO_4 (5 ml) is added and the soln. is heated to boiling-point. The $BaSO_4$ is filtered off and the filtrate is diluted to 100 ml. To a 10-ml aliquot is added 25 ml of buffer soln. at pH 4·7 and 10 ml of HIO_4. After 30 min. the excess of HIO_4 is determined by adding 0·04 N As_2O_3 (20 ml), KI soln. (1 ml) and an excess of $NaHCO_3$, and titrating with 0·01 N iodine. A blank test is carried out at the same time.

J. V. Russo

2349. **Rapid determination of dry matter in emulsion liqueurs on filter-paper and aluminium foil with the use of infra-red radiation.** J. Kottász (State Inst. for Chem. and Food Exam., Budapest, Hungary). *Z. LebensmittUntersuch.*, 1958, **108** (5), 441–442.—The samples (egg-brandy or chocolate flip) are delivered dropwise on to a double layer of dried filter-paper, supported on aluminium foil, from a series of wide-mouthed pipettes (3 ml) which are bent at an angle for convenient support on a weighing-stand (*cf.* Schulz *et al.*, *Milchwissenschaft*, 1957, **12**, 291). Care must be taken to avoid the coalescence of the drops on the filter-paper. Drying is completed by the use of infra-red radiation. The results agree well with those obtained by drying under similar conditions in a platinum dish.

P. S. Arup

2350. **Gas-phase chromatography. General description and applications to the detection of adulteration.** P. Chovin (Municipal Lab., Paris). *Ann. Falsif.*, 1958, **51**, 253–268.—A general description of the physical principles of the method is given, which includes the calculations of retention time and vol. in terms of pressure applied. The method can be applied to the separation of straight-chain

saturated and unsaturated fatty acids and their methyl esters. Analysis of the methyl esters of the fatty acids of olive oil before bromination showed traces of 11 acids and two main peaks corresponding to palmitic and oleic acids and one minor peak of a C_{19} acid, branched or unsaturated. Analysis of the brominated acids revealed the presence of palmitate, stearate and a branched C_{18} acid. Similar analysis of the fatty constituents of horse milk showed 19 saturated acids before the myristic acid peak and 8 new acids between the myristic and stearic acid peaks. S. BAAR

2351. **Testing of fats and oils by the critical mixing temperature.** R. Fischer and T. Kartnig (Graz Univ., Austria). *Fette, Seif., Anstrichmitt.*, 1958, **60** (10), 904–906.—The critical mixing temp. (CMT) of various fats and oils with a range of org. liquids have been determined. The degree of adulteration of butter with arachis oil, or of lard with cottonseed oil, may be estimated to within 2·5 to 3% using diethyl sulphate or acetonyl-acetone. For 40 samples of lard and 20 samples of beef tallow examined, the relationship iodine value $= K - (3{\cdot}12\ \text{CMT})$ was found to hold, where K is a constant depending on the system. With propyl cyanide, $K = 206{\cdot}3$ and $205{\cdot}4$, and with 2-ethoxyethanol, $K = 197{\cdot}3$ and $196{\cdot}2$ for the two fats, respectively. L. A. O'NEILL

2352. **Improved saponification-number determination by means of ion exchange.** W. B. Swann, R. J. Zahner and O. I. Milner (Socony Mobil Oil Co., Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1830–1833.—The procedure described ensures a very sharp end-point and does not require precautions to prevent absorption of CO_2 during transfer and titration. The sample ($\equiv$ 0·5 to 1·5 milli-equiv. of saponifiable matter) is boiled under reflux for 2 hr. with 15 ml each of ethanolic 0·2 *N* KOH and benzene. The saponified soln. is passed through a 50-cm column of Amberlite IR-120 (H form) at the rate of $\simeq$ 2 ml per min., the resin being washed finally with benzene - ethanol (1 : 1). The weak organic acids in the eluate ($\simeq$ 120 ml) are then titrated potentiometrically with 0·2 *N* KOH. Well-defined inflections and high accuracy are attained for acids having dissociation constants $< 10^{-7}$. W. J. BAKER

2353. **A simple method of separating the unsaturated fraction from small amounts of lipids.** F. Leupold and D. Eberhagen (Med. Univ. Klinik, Köln, Germany). *Fette, Seif. Anstrichmitt.*, 1958, **60** (9), 809–811.—The method is based on the formation of inclusion compounds of urea with fatty acids in an organic solvent (*cf.* Bengen and Schlenk, *Experientia*, 1949, **5**, 200). From mixtures containing an overwhelming proportion of saturated and only weakly unsaturated fatty acids, such as human serum, it was possible to obtain, by crystallisation at $-$ 20°, a fraction sufficiently enriched in pentaene and hexaene acids to be utilisable for u.v. spectrophotometry. The results compare favourably with the low temp. fractional crystallisation method of Shinowara and Brown (*J. Biol. Chem.*, 1940, **134**, 331), it is more rapid and the weight required for the determination is one-twentieth. A. TESSLER

2354. **Paper chromatography of fats. XXVIII. The separation of thiocyanated fatty acids.** H. P. Kaufmann and M. Arens (Inst. f. Pharm. u. Lebensmitt. Chem., Univ., Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (9), 803–806.—Attention is called to the usefulness of the thiocyanated fatty acids obtained as by-products of the routine determination of the thiocyanate value. Their R_F values differ considerably from those of the unsaturated fatty acids from which they are derived and whose position on the chromatogram coincides with that of certain saturated fatty acids (the "critical" pairs, *e.g.*, palmitic and oleic acids). It was thus possible, by submitting these derivatives to paper chromatography, to effect a more rapid identification of the constituent fatty acids than would be possible by means of the usual methods of qual. analysis. By varying the strength of the acetic acid in the acetic acid - undecane system employed, an additional selective effect was achieved. A quant. determination was also feasible by subjecting chromatograms obtained before and after thiocyanation to photometry. A. TESSLER

2355. **Paper-chromatographic examination of thiocyanated fatty acids.** W. Awe and B. Grote (Inst. f. angew. Pharm. d. Tech. Hochschule, Braunschweig). *Fette, Seif., Anstrichmitt.*, 1958, **60** (9), 806–809.—The properties of thiocyanated fatty acids and their significance from the point of view of qual. and quant. analysis of fats are reported, resulting from work carried out independently of Kaufmann and Arens (*Anal. Abstr.*, 1959, **6**, 2354) with substantially identical findings. A. TESSLER

2356. **Analytical separation of the methyl esters of the C8 to C34 straight-chain fatty acids and the detection of odd-carbon-number acids in commercial mixtures of fatty acids by gas chromatography.** M. A. Kahn and B. T. Whitham (Shell Res. Ltd., Thornton Res. Centre, Chester, England). *J. Appl. Chem.*, 1958, **8** (9), 549–552.—The work described has been carried out on conventional equipment fitted with a katharometer designed to operate up to 300°. The retention vol. of the esters of the C_{18} to C_{34} acids relative to methyl stearate are listed. K. A. PROCTOR

2357. **Differentiation between rectified olive oil A and oil regenerated from distilled fatty acids.** V. Sossi (R.I.O., Imperia, Italy). *Olii Min.*, 1958, **35** (9), 335–337.—The possibility of differentiating between rectified olive oil A and oils prepared by esterification of fatty acids (from olive or other oils of vegetable or animal origin) by means of chemical and physical constants has been examined. The hydroxyl value is usually higher for the re-esterified oils, but no other single determination gives a clear distinction. The combined results, however, can give a useful indication of the source of the oil. L. A. O'NEILL

2358. **Determination of palm-kernel oil in cacao butter by partition chromatography.** W. Wachs and P. Petscha (Inst. Lebensmittel-chem. u.-technol., Tech. Univ., Berlin-Charlottenburg). *Z. Lebensmittlntersuch.*, 1958, **108** (3), 244–255.—The method depends on the determination of lauric acid in the hydrogenated fatty acids. The acids (60 mg) dissolved in the initial solvent (5 ml) at 50° are deposited on a column of kieselguhr that has been made water-repellent by treatment with dimethyldichlorosilane; the acids are separated by elution with mixtures of water and acetone (saturated with liquid paraffin) of progressively increasing content of acetone as the separation

proceeds. The eluate flows into a vessel from which 2-ml portions are successively siphoned into a vessel in which they are titrated under nitrogen with 0·01 *N* NaOH. The relative proportions of the acids, especially those in the C_{12} and C_{14} range, are calculated from the mol. wt. (depending on the composition of the eluent) and the titration equiv. The method allows of the detection of 1% of palm-kernel oil, and is subject to an error of 8% in the range 1 to 5%. In analysing cacao-butter substitutes, a 30-mg sample is treated similarly (*cf. Fette, Seif., Anstrichmitt.*, 1958, **60**, 655).

P. S. ARUP

2359. **Absorption spectra of technical waxes and their components in the infra-red and ultra-violet regions.** W. Fuchs and G. Addicks (Tech. Hochschule, Aachen, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (10), 907–909.—Higher fatty acids (C_{16-31}), as found in waxes, may be differentiated by the relationship between the number of C atoms (N) and the number of maxima (M) in the i.r. spectrum region 7·43 to 8·47 μ—when N is even, $M = (N + 2)/2$, when N is odd, $M = (N + 1)/2$. For esters of the acids with higher alcohols, relationships similarly hold with the number of C atoms in the fatty acid chain, independent of the length of the alcohol chain and, in this case, when N is even, $M = (N + 2)/2$, but when N is odd, $M = (N + 3)/2$. The spectra are determined by the KBr pellet technique and are not significantly affected by up to 10% of impurities consisting of other wax acids, esters or alcohols.

L. A. O'NEILL

2360. **Some paper-chromatographic studies on vitamins D.** A. Mayer, C. W. Picard and F. Wokes (Ovaltine Res. Lab., King's Langley, Herts.). *Pharm. Acta Helv.*, 1958, **33** (8–9–10), 603–620 (in English).—Chromatography on paper impregnated with liquid paraffin for the separation of μg-quantities of vitamins D for subsequent spectrophotometric determination has been studied. To minimise instability of the vitamins during the procedure, it is necessary to work with quantities of $\simeq$ 100 μg, to avoid exposure to light or heat, to keep the developed chromatograms moist until elution is complete, and to allow the impregnated paper to "age" for 2 to 8 days before use. Spectrophotometric evidence for degradation of the vitamins during chromatography is presented. Experiments with cholecalciferyl-4-^{14}C butyrate indicate that incomplete elution can be a further factor affecting the recovery.

A. R. ROGERS

2361. **Estimation of vitamin C in coloured preparations.** B. Sarkar, M. Sharma and G. K. Ray (Central Drug Res. Inst., Lucknow). *Indian J. Pharm.*, 1958, **20** (8), 214–216.—Ascorbic acid (**I**) reduces $HgCl_2$ to HgCl, which is then determined iodimetrically. To an aliquot of test soln. (20 to 30 mg of **I**) add 25 ml of 0·01 *N* $HgCl_2$, and heat on a water bath for 5 min. Cool, and allow to stand for 45 min. Add 5 ml of 2 *N* $BaCl_2$, filter, wash the ppt. and dissolve it in 30 ml of 0·01 *N* iodine. Back-titrate the excess of iodine with 0·01 *N* $Na_2S_2O_3$. Recoveries of 0·025 g of **I** added to three prep. ranged from 99·7 to 100·0%.

R. E. ESSERY

2362. **Interfering substances in the determination of ascorbic acid in food products.** L. Nevařil (Východoslovenské Konzervárny n.p., Sabinov, Czechoslovakia). *Průmysl Potravin*, 1958, **9** (8), 441–442.—Compounds of the reductone type (reductonic acid, reductone, hydroxytetronic acid), compounds with SH groups (glutathione and its derivatives, cysteine), SO_2 and natural organic dyes cause interference when determining ascorbic acid by means of the common methods. The author discusses various newer methods which make this determination possible even in the presence of interfering substances.

J. ZÝKA

See also Abstract—**2208**, Fructose in orange and persimmon juices.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

2363. **Colorimetric method for continuous recording analysis of atmospheric sulphur dioxide.** H. L. Helwig and C. L. Gordon (State Dept. Public Health, Berkeley, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1810–1814.—The SO_2 in the air (rate of flow 250 ml per min.) is absorbed in the reagent (rate of flow 3·3 ml per min.), and the extinction of the coloured complex is measured at 560 mμ in a 2·5-cm cell. Aspiration and measurements are carried out in a Kruger conductimetric analyser modified to contain cell, mercury lamp, syncroverter and automatic recorder. The reagent is a 0·04% (w/v) soln. of para-rosaniline hydrochloride in 10% (v/v) HCl, 40 ml of which is mixed with 2 litres of a 0·02% (v/v) soln. of formaldehyde in HCl and the pH adjusted to 1·5. The presence of formaldehyde increases the stability and rate of development of the colour and is preferred to the sodium tetrachloromercurate used by West (*cf. Anal. Abstr.*, 1957, **4**, 1817). Beer's law is valid for concn. of SO_2 from 0·01 to 5 p.p.m., but by varying the rates of flow of air and reagent these limits can be extended or reduced. The sensitivity is 0·002 μg of SO_2 per ml of reagent at low concn. Ozone ($\gtrsim$ 2 p.p.m.) and NO_2 ($\gtrsim$ 1 p.p.m.) cause negligible interference.

W. J. BAKER

2364. **Determination of low concentrations of methane in coal-mine-air samples by infra-red absorption spectrometry.** F. J. Colbassani and H. A. Watson. *Inform. Circ. U.S. Bur. Min.*, 1958, No. 7839, 13 pp.—Under the conditions described, other gases in low concn. show no interference. Strongest absorption occurs at 7·66 μ, but the increase with methane concn. is not linear. An empirical calibration is used in the evaluation. Absorbance measurements and analysis were simultaneously carried out at the same preselected gas pressure in a gas cell. Apparatus and calibration procedure are described and data relating to CO_2 and ethane given.

S.C.I. ABSTR.

2365. **Colorimetric determination of diphenyl bases in the air of factories.** P. Engelbertz and E. Babel. *Zentr. Arbeitsmed. u. Arbeitsschutz*, 1957, **7**, 211–212.—One-hundred litres per hr. of air is sucked through absorption vessels each filled with 10 ml of ethanediol (**I**). The absorbent soln. (5 ml) is mixed with 45 ml of 96% acetic acid, 0·25 ml of a 10% soln. of *p*-dimethylaminobenzaldehyde in 96% acetic acid is added, and the yellow colour developed is determined photometrically. The following detectable minimum concn. of diphenyl bases in **I** are given (in parentheses the minimum vol. of **I** necessary for dissolving 1 g of diphenyl

base)—benzidine 2×10^{-7} (4 ml), 2:2′-dichlorobenzidine 2×10^{-6} (16 ml), *o*-tolidine 1×10^{-7} (10 ml), *o*-dianisidine 1×10^{-7} (20 ml), and 2:2′-dichloroanisidine 1×10^{-7} (32 ml).

CHEM. ABSTR.

2366. **Glass-fibre filter medium in the suspended solids determination.** G. Chanin, E. H. Chow, R. B. Alexander, and J. Powers (East Bay Municipal Utility District, Oakland, Calif.). *Sewage Ind. Wastes*, 1958, **30** (8), 1062–1066.—A method is described for the determination of suspended solids of sewage samples; a sample vol. of 25 ml is recommended with the filters used (fine borosilicate-glass fibres). Some difficulties of Gooch crucible mat preparation are discussed, and the test time is reduced. O. M. WHITTON

2367. **New method for determination of suspended solids.** I. Nusbaum (Water Pollution Control Board No. 9, San Diego, Calif.). *Sewage Ind. Wastes*, 1958, **30** (8), 1066–1069.—The test results reported show that glass-fibre filter-discs provide a medium which does not have the main disadvantage of paper, *i.e.*, hygroscopicity, and that a wire-cloth disc-support is an aid to a rapid vacuum-filtration technique. O. M. WHITTON

2368. **Direct method of determining carbon dioxide tension.** W. F. Loomis (The Loomis Lab., Greenwich, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1865–1868.—A method for measuring the pCO_2 of 10-ml samples of water is based on equilibrating the sample with an equal vol. of CO_2-free air. A Haldane - Henderson gas-analysis apparatus is used to determine the CO_2 content of the air, and a correction is applied to allow for absorption of CO_2 by the water at the temp. of the measurement. It is accurate to about $\pm$ 0·01% atm. over the range 0·0 to 110 mm of mercury (0 to 15% atm.).

G. P. COOK

2369. **Concentration and determination of traces of silver, copper, lead, zinc (and nickel) in natural waters.** V. B. Aleskovskiĭ, A. D. Miller and E. A. Sergeev. *Trudy Komiss. Anal. Khim., Akad. Nauk SSSR*, 1958, **8** (11), 217–226; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,348.—Two methods are used for the concentration of traces in the determination of Cu, Ag, Pb and Zn in natural waters—co-pptn. with $CaCO_3$ with subsequent dissolution of the ppt. in a small vol. of acid, and the method of "sinking particles." The latter method is based on the fact that particles of a cation-exchange resin of sufficiently small size sink and so traverse the whole vol. of a stationary soln. By suitable choice of the particle size and amount of the resin, it is possible to extract the traces completely from the soln. in a short time. The completeness of the extraction, other things being equal, depends mainly on the particle size of the resin, the amount of resin used, and the original concn. of the element. For the concentration of Cu with a resin-particle size of 100 to 150 μ, 10 g of resin is required for complete extraction. The presence of up to 20 mg of Fe per litre does not cause interference in the determination of Cu. When using co-pptn. with $CaCO_3$ to concentrate the traces, complete co-pptn. of Cu is achieved with a ppt. of $\simeq$ 0·5 g, and of Pb with a ppt. of $\simeq$ 0·1 g. More or less complete co-pptn. of Ag takes place only in the presence of Fe^{3+}; Fe^{3+} do not interfere in the determination of Pb at concn. up to 10 mg per litre. The minimum concn. of the elements which may be determined after concentration by these methods are Ag 10, Cu 5 to 10, Pb 5 to 10, and Zn 5 to 10 μg per litre. Nickel may also be concentrated by the sinking particle method, and then determined photometrically with dimethylglyoxime. C. D. KOPKIN

2370. **A field test for radioactive strontium and barium in water under emergency conditions.** A. R. Agg, G. E. Eden and K. V. Melbourne. *Proc. Soc. Wat. Treatm. Exam.*, 1957, **6**, 142–154.—The principal hazard in drinking water containing fission products is due to the ingestion of ^{89}Sr and ^{140}Ba, and a method has therefore been devised for the direct determination of these isotopes in the field, using a minimum of equipment. The method involves filtration of the sample, if necessary, and passage through a small ion-exchange column filled with Zeo-Karb 225, in which only the activities due to Zr, Nb, Y, rare-earth elements, Sr and Ba are retained. The unwanted activities are selectively eluted with a suitable reagent such as ammonium citrate soln., and the activities due to Sr and Ba are then eluted with a soln. of EDTA for assay in a water monitoring tube. The ion-exchange material is decontaminated and prepared for further use by washing with water. The apparatus used is illustrated. WAT. POLLUT. ABSTR.

2371. **Analysis for zinc, cadmium and copper in electroplating waste effluents.** F. Stevens and L. E. Lancy (Lancy Lab., Zelienople, Pa., U.S.A.). *Plating*, 1958, **45** (8), 832–834.—From 0·5 to 50 p.p.m. of Zn and Cd can be determined, in the presence of Cu, Fe and Ni, by titration of the sample (100 ml, containing NaCN and ascorbic acid) with 0·01 or 0·001 *M* EDTA (disodium salt) after adding formaldehyde soln. (1:1) (5 ml) to demask the Zn and Cd. The Cd in a similar aliquot is then pptd. with Na_2S in the presence of an excess of NaCN, and the Zn alone is titrated with EDTA to obtain the Cd by difference. The indicator is Eriochrome black T. From 0·1 to 5 p.p.m. of Cu can be detected semi-quant. by the addition of a 0·05% (w/v) soln. of 1-(2-pyridylazo)-2-naphthol (PAN) to the buffered sample, the intensity of the pink coloration being approx. proportional to concn. of Cu; Zn, Cd, Ni, Fe and Hg, even at concn. of 10 to 15 p.p.m., do not interfere. Provided that $Fe(CN)_6^{4-}$ and Hg are absent, from 0·02 to 0·5 p.p.m. of Cu in 100 ml of soln. can be determined spectrophotometrically to within $\simeq$ 1% as the neocuproin complex at 460 mμ (*Anal. Abstr.*, 1957, **4**, 361). When $Fe(CN)_6^{4-}$ are present, they should be eliminated by treatment with $HgCl_2$ before the addition of neocuproin soln. The extracted neocuproin complex is then destroyed with HNO_3 plus H_2SO_4 (boiling) and the Cu in the neutralised and buffered soln. is titrated at $\simeq$ 70° with 0·01 *M* EDTA (PAN as indicator) after masking Hg with KI. The error is from 5 to 10%. W. J. BAKER

2372. **Rapid screening test for cadmium in potable water.** M. Lieber (Nassau County Dept. Health, Hempstead, N.Y.). *Wat. & Sewage Wks*, 1958, **105** (9), 374.—Dithizone reagent is added to prepared standards representing 0·0, 0·1, 0·2, 0·3 and 0·4 p.p.m. of Cd and to a 50-ml sample in a Nessler tube, and after 5 min. comparisons are made visually. Interference is caused by Cu^{2+} and Ni^{2+} but not by Cr^{6+}. O. M. WHITTON

2373. **Determination of sulphates in drinking and surface waters.** J. Čuta and J. Hanušová. *Coll. Sci. Rep.*, 1952–1955, *Inst. Hyg. Prague*, 1957,

(8–9).—Two methods have been developed for the volumetric determination of SO_4^{2-} in surface and drinking waters. The first involves heating the sample of water with excess of $BaCl_2$ and determining the Ba^{2+} by titration with EDTA (disodium salt), with phthalein complexone as indicator. The second method involves direct titration of the SO_4^{2-} with thorium nitrate using, as indicator, 2-(*o*-carboxyphenylazo)-1:8-dihydroxynaphthalene-3:6-disulphonic acid, which has a colour change from pink to violet at the end-point.

WAT. POLLUT. ABSTR.

2374. **Rapid method for the determination of sulphates.** F. Karas, J. Eliášek and V. Palatý (School of Chem. Technol., Prague). *Voda*, 1958, **37** (10), 316–317.—A modification of the use of thoron [1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid] as metallochromic indicator (Fritz and Yamamura, *Anal. Chem.*, 1955, **27**, 1461) is described. *Procedure*—Pass the sample containing dissolved sulphate through a cation-exchange column (Wofatit KPS-200), discard the first 10 ml of the eluate, and to another 10 to 25 ml add $HClO_4$ or NaOH till the pH is 3 to 5 and *iso*propyl alcohol in excess; add indicator soln. (0·2% aq. soln.) (2 to 4 drops) and titrate the yellow soln. with 0·01 to 0·05 *N* $Ba(ClO_4)_2$ (in 80% *iso*propyl alcohol) till pink. The method yields good results for the determination of sulphates in water, fuels or coal (after combustion and oxidation) and in biological materials.

J. ZÝKA

2375. **Chelatometric determination of sulphates in water, with calcein as indicator.** M. Effenberger (Inst. Technol. of Water, High School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (8), 1501–1505.—The indirect complexometric determination is based on the pptn. of SO_4^{2-} as $BaSO_4$ and titration of the excess of Ba^{2+} with EDTA (disodium salt), with calcein as indicator. The method is suitable for determining SO_4^{2-} over a wide range of concn. The interference of heavy metals can be avoided by the addition of triethanolamine and KCN. *Procedure*—First determine the content of Ca in 100 ml of the sample with the use of 0·02 *M* EDTA (disodium salt) after addition of *M* KOH (5 ml) and about 0·07 g of calcein (mixed 1:100 with NaCl). When interfering ions are present, add a suitable amount of triethanolamine and KCN. To another portion of the sample (100 ml) add a vol. of 0·1 *N* HCl equal to that consumed in the determination of the alkalinity of the sample (methyl orange as indicator) and 5 ml of 0·1 *N* HCl in excess. Boil and add a suitable amount of 0·005 *M* to 0·02 *M* $BaCl_2$ (according to the amount of SO_4^{2-}). Boil for 2 min., set aside for 20 min. on the water bath and filter off the $BaSO_4$ with a paper filter. Wash the ppt. with 20 ml of hot H_2O, cool the filtrate, add *M* KOH (5 ml), and triethanolamine and KCN when necessary, and titrate with EDTA soln. (disodium salt).

J. ZÝKA

2376. **Determination of small quantities of surface-active polyglycol derivatives in water.** H. Etienne. *Bull. Centre Belge Étud. et Document. Eaux*, 1958, (40), 159–166.—The method, by which 0·2 p.p.m. can be determined, consists essentially in pptn. with molybdophosphoric acid, treatment of the ppt. with HI, conversion of the ethyl iodide so produced into ethyl bromide, and determination of the liberated HIO_3. A special apparatus is required, of which a dimensione drawing is given. The water, containing 1 mg of potential ethylene oxide, is evaporated to 100 ml and cooled. It is then treated with 6 *N* HCl to neutrality and 10 ml in excess, then successively with 10 ml of 10% $CaCl_2$ soln., ≃ 200 mg of Celite, and 10 ml of 10% molybdophosphoric acid soln. The mixture is boiled, allowed to stand overnight, and centrifuged at 3500 r.p.m. for 5 min. The ppt. is washed in the centrifuge, suspended in a little water, and introduced into the special double-tubulured reaction vessel, in which it is dried in a stream of air, washed twice with light petroleum to remove interfering fatty matter, and dried again. Hydriodic acid (3 ml, *d* 1·7) is introduced into the reaction vessel, both tubulures are sealed, and the vessel is heated at 130° to 140° for 12 to 15 hr. After cooling in solid CO_2 for 30 min., the reaction vessel is attached to the apparatus, after breaking the seals, in a specified manner, and heated in a glycerol bath at 120°; a stream of CO_2 (washed with 0·1 *N* $AgNO_3$ and conc. H_2SO_4) is passed for 3 to 4 hr., and carries the ethyl iodide through a suspension of red phosphorus (0·5 g in 5% aq. $CdSO_4$ soln.) into an absorber containing 15 ml of bromine soln. (prepared at the moment of use by dissolving 0·5 ml of Br, free from iodine, in 14·5 ml of a soln. prepared by dissolving 100 g of anhyd. K acetate in a mixture of 900 ml of glacial acetic acid and 100 ml of acetic anhydride). This converts ethyl iodide into ethyl bromide and HIO_3. The bromine soln. is washed into a flask containing 3 ml of 10% Na acetate soln., diluted to 30 ml, and decolorised with 90% formic acid, allowed to stand for 3 min., then 1 g of KI and 5 ml of 10% H_2SO_4 are added and the iodine is titrated with 0·05 *N* $Na_2S_2O_3$. A blank (1 litre) of potable or distilled water is treated simiarly. The method is satisfactory for balanced or hydrophilic polyglycolic ethers, and also for lipophilic ones if the washing with light petroleum can be dispensed with. It is less generally applicable to polyglycolic esters.

R. E. ESSERY

2377. **The action of detergents of different ionic activity in the methylene blue method of determination.** W. Husmann, W. Schoch and G. Thomaschk. *Vom Wasser*, 1957, **24**, 160–170.—Experiments are described which were made to determine the reactions of different detergents in the methylene blue method of determination, the constituents of anionic substances affected, and the influence of cationic and non-ionic substances on the determination of anionic detergents. In general the results, details of which are given in tables and graphs, show that all anionic substances have a positive reaction by the methylene blue method, cationic substances produce no $CHCl_3$-sol. methylene blue complex, and non-ionic detergents, in amounts appearing in practice in sewage, do not react. In the anionic detergents, only the anionic fraction and not the total active substance was determined. Results were affected by the presence of detergents of different ionic activity; the effect was not proportional. An additive effect was found on addition of non-ionic detergents, in amounts greater than those normally found in sewage, to anionic substances, but the values obtained were those of the anionic fraction and not the total active substance.

WAT. POLLUT. ABSTR.

See also Abstracts—**2114**, Determination of SO_4^{2-} in waters. **2218**, Determination of hexamethylene di*iso*cyanate in air.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

2378. **Rapid method for the determination of adsorbed calcium and magnesium in soil.** T. F. Astafurova and A. A. Temkina. *Trudy Altaisk. Sel'sk. Inst.*, 1957, (5), 124–130; *Ref. Zhur., Khim.*, 1958, (22), Abstr. No. 73,698.—Calcium and Mg adsorbed in soil are completely extracted with a soln. of $NaNO_3$, and are subsequently determined complexometrically. To an aliquot of the extract, containing 1 to 10 mg of Ca, add 100 ml of water and 2 ml of 10% NaOH soln. and titrate Ca with 0·05 *M* EDTA (disodium salt), with murexide as indicator, till the colour changes from pink to lilac. Then add to the same soln. 2·5 ml of 10% HCl [to destroy the murexide colour and dissolve $Mg(OH)_2$; the soln. is decolorised in 1 or 2 min.], 15 ml of buffer soln. (20 g of NH_4Cl and 100 ml of 25% aq. NH_3 per litre), and a soln. of Eriochrome black T (0·5 g of indicator dissolved in 30 ml of buffer soln. and diluted to 100 ml with ethanol), and titrate Mg with EDTA (disodium salt) till the colour changes from pink to blue. The analysis takes 3 to 4 hr.; the error is 5 to 6%. C. D. KOPKIN

2379. **The determination of the alkali requirement (CaO) of acid agricultural soils from an estimation of the pH and the methylene blue adsorption value.** H. Peter and S. Markert (Inst. f. Landwirtschaftl. Versuchs- und Untersuchungs-wesen, Leipzig, Germany). *Naturwissenschaften*, 1958, **45** (24), 625.—From a knowledge of the soil pH and methylene blue adsorption the alkali requirement can be calculated. From tables published elsewhere (*Z. landw. Versuchs- u. Untersuchungswes.*, 1956, **1**, 582) the amount of alkali can be calculated that is required to adjust the pH of the soil to a predetermined value. The mean variation in over 1000 laboratory tests was ± 0·4 pH unit. E. KAWERAU

2380. **Rapid determination of water-soluble phosphorus pentoxide in superphosphate and total phosphorus pentoxide in dicalcium phosphate.** S. Harel, M. Tamari and A. Talmi (Fertilizers and Chemicals Ltd., Haifa, Israel). *J. Agric. Food Chem.*, 1958, **6** (8), 589–591.—Water-sol. phosphate in a superphosphate extract [containing free H_3PO_4 and $Ca(H_2PO_4)_2$] is determined to within ± 1% in 5 min. by titrating with NaOH soln. to a grey colour with a mixed indicator containing methyl red, bromocresol green and cresol purple; at this pH (4·9), the free H_3PO_4 is converted into the primary salt; K oxalate is then added to precipitate Ca oxalate, and make possible a further titration with NaOH soln. to a purple - red colour at pH 9·3, when the primary salt is converted into the secondary salt. The amount of NaOH used is equivalent to the H_3PO_4 content. The second end-point is determined by comparison with an extract of superphosphate containing a known amount of phosphoric acid titrated to the first end-point and then neutralised with the theoretical amount of NaOH soln. The method can also be applied to the determination of total H_3PO_4 in dicalcium phosphate. M. D. ANDERSON

2381. **Colorimetric determination of phosphoric acid in fertilisers by the molybdovanadophosphate method. I. Studies on the colour reagent.** Minori Matsubara (Sumitomo Chem. Ind., Niihama, Ehime-ken). *Japan Analyst*, 1958, **7** (8), 505–509.—The effect of the composition of a mixture of ammonium molybdate, metavanadate and HNO_3 on the colorimetric determination of P (*cf.* Quinlan and DeSesa, *Anal. Abstr.*, 1956, **3**, 380) was examined with respect to the analysis of fertilisers. When P (< 8 mg of P_2O_5 per 100 ml) is to be determined in HNO_3 (0·5 *N*), the molar ratio of Mo to P must be > 22 and of V to P > 1·7. In the presence of citric acid (*e.g.*, 0·34 g by the use of Peterman's method; HNO_3 concn. ≃ 0·7 *N*), the molar ratio of Mo to P must be > 27 and of V to P > 1·7. K. SAITO

2382. **Determination of diphenylamine residues on apples.** R. B. Bruce, J. W. Howard and J. B. Zink (Hazelton Lab., Falls Church, Va., U.S.A.). *J. Agric. Food Chem.*, 1958, **6** (8), 597–600.—Diphenylamine, used to control scald in apples, is determined by mixing apple samples with 90% methanol, extracting the slurry with light petroleum, extracting the diphenylamine into conc. HCl as the hydrochloride, and diluting with water to give the free amine, which is re-extracted into light petroleum and measured colorimetrically by treating with diazotised 2:4-dinitroaniline and methyl cyanide, adding H_3PO_4, and reading the extinction at 530 mμ. Figures are given for diphenylamine residues on apples dipped in diphenylamine, and on those stored in diphenylamine wraps. M. D. ANDERSON

2383. **Absorptiometric analysis of N-(trichloromethylthio)*cyclo*hex-4-ene-1:2-dicarboxyimide (captan).** H. P. Burchfield and J. Schechtman (Boyce-Thompson Inst. for Plant Res. Inc., Yonkers 3, New York). *Contr. Boyce Thompson Inst.*, 1958, **19** (5), 411–416.—The method described is applicable to soils. The soil is extracted with dichloromethane, and the extract is decolorised by treatment with Norit and Florisil. After evaporation of the solvent, the residue is treated with a mixture of pyridine and tetraethylammonium hydroxide and the intensity of the coloration formed is measured at 415 mμ. Colour stability is good in the presence of the quaternary hydroxide, but is very poor when NaOH is used. The extinction is measured within 2 min. after addition of the reagents, but the colour is stable for ≃ 30 min. The related fungicide, phaltan, is determined similarly. J. N. ASHLEY

2384. **Determination of diethyl *p*-nitrophenyl phosphate (Mintacol solubile) [Paraoxon].** J. Blažek (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (8), 455–456.—A rapid method is based on a reduction of the nitro group to an amino group followed by potentiometric titration. *Procedure*—A sample (corresponding to ≃ 16 mg of Mintacol) is weighed accurately into a 250-ml flask, dilute HCl (25 ml) and powdered zinc (2 g) are added, and the mixture is boiled under reflux for 15 min. After filtration, the flask is washed with more HCl (20 ml), and fuming HCl (20 ml) and KBr (1 g) are added to the filtrate. The soln. is titrated slowly with 0·01 *M* $NaNO_2$ at 15° to 20° until the deflection of the galvanometer is constant. A system of two electrodes (platinum and graphite) connected directly to a galvanometer is recommended. The mean error is ± 2%. J. VOLKE

See also Abstracts—**2099**, Determination of ^{230}Th in soil air. **2188**, Application of radio-indicators to determination of pesticides. **2209**, Determination of hemicelluloses in forage crops. **2220**, Determination of dithiocarbamic acid derivatives in anticryptogams.

5.—GENERAL TECHNIQUE AND APPARATUS

General

2385. **Burette for titrants requiring an inert atmosphere. Application to quadrivalent uranium solutions.** D. J. McEwen and T. De Vries (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1889.—The borosilicate-glass burette described and illustrated can be used to store and dispense soln. of, *e.g.*, 0·01 *M* $U(ClO_4)_4$ in 0·1 *M* $HClO_4$, or water-sensitive soln. of organoaluminium compounds. The method of filling and sealing is simple. W. J. BAKER

2386. **Derivatographic micro-distillation for the examination of liquid mixtures.** F. Paulik, L. Erdey and S. Gál (Inst. für allg. Chem., Tech. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1958, **163** (5), 321–329.—Based on the method previously reported (Paulik *et al.*, *Anal. Abstr.*, 1958, **5**, 4379), experiments have been carried out on binary and ternary mixtures and the data illustrated by means of thermograms. This micro-method is suitable for the distillation of small amounts of petroleum or its derivatives, and essential oils. The automatic registration of thermo-gravimetric curves gives an accurate picture of the whole distillation procedure. Reliable results are obtained with quantities of 1 to 0·5 g or much smaller. B. B. BAUMINGER

2387. **Liquid - liquid extraction: efficiency of a perforated-plate pulsed column.** B. Choffé and Y. L. Gladel (Inst. Français du Pétrole, Rueil-Malmaison, Seine et Oise, France). *J. Appl. Chem.*, 1958, **8** (9), 580–586.—Increased efficiency of extraction can be obtained by the application of a pulse to a perforated-plate, liquid - liquid, counter-current extraction column. The rates of liquid flow, pulse amplitude and frequency have been studied for their effect on the efficiency of extraction. K. A. PROCTOR

2388. **Automatic apparatus for removing polar compounds from water-immiscible solvents.** J. Klimeš (Výzk. Ústav Krmivářský, ŠSZV, Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (8), 1650–1652.—The apparatus is based on a series of jets, so that the extracted mixture can be intensively washed and mixed with water. Intensive contact of both liquids and a rapid extraction are thus achieved. Two modifications of the apparatus, for liquids heavier and lighter than water, are described. The suitability of the apparatus has been tested by the determination of carotene. It was found that by removing acetone from a solvent mixture with benzene (1:1) containing 50 to 500 μg of carotene in 200 ml, no loss of carotene was observed during the procedure. J. ZÝKA

2389. **Polyethylene filters for laboratory use.** E. G. Heath (London and Scandinav. Metallurgical Co., Ltd., London, S.W.8). *Chem. & Ind.*, 1958, (34), 1111–1112.—Polyethylene powder of 80 to 100 mesh may be used in a Hirsch or other highly porous glass-disc funnel, as a film, if it is applied as a slurry in ethanol or aq. ethanol and then gently sucked dry. The film is not attacked by alkalis and such a filter has been made inside polyethylene tubing, on a polyethylene disc, for operations with HF. E. G. CUMMINS

2390. **Slide rule for calculation of titrimetric curves.** J. Čeleda (Inst. Inorg. Chem., High School of Chem. Technol., Prague). *Chem. Průmysl*, 1958, **8** (4), 173–175.—The simple construction of a slide rule suitable for the rapid calculation of figures for titrimetric consumption which are dependent on pH values and based on the method for computing neutralisation curves [*Ibid.*, 1958, **8** (3, Add. I), 1] is described. The rule has a stable scale of pH values against which sliders are moved, involving values of the function $10^{n \cdot pH}$, and indicating the "partial consumption" of every component present. Titrimetric consumption at any chosen pH value is estimated by adding up the data on all sliders against the pH value given, and adding the sum total to the stoicheiometric consumption at the equiv. point. The share of every component at total consumption can be read directly on this rule, and the origin and the magnitude of the theoretical titrimetric fault at any pH value may be determined. J. ZÝKA

2391. **Oxygen lamp for determination of sulphur in fuel gas.** D. McA. Mason and C. E. Hummel (Inst. Gas. Technol., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1885–1886.—An oxygen lamp is described which is more convenient and reliable than the air lamp, especially when a variety of gases is analysed. Neither gas nor oxygen rate requires critical adjustment. Results obtained with the oxygen lamp agreed with those obtained from an air lamp, within 0·2 grain of S per 100 cubic ft. or within 3% for a high-sulphur gas. G. P. COOK

Chromatography, ion exchange, electrophoresis

2392. **Switch unit for collecting small fractions from chromatographic columns.** K. Blau and M. F. Fordom (King's College, Univ. of London). *Chem. & Ind.*, 1958, (34), 1112.—The scale diagram illustrates the siphon-operated beam and micro-switch which control the current for the operation of the fraction collector. The siphon is adjustable from 1 to 25 ml capacity. E. G. CUMMINS

2393. **Five-part mechanically operated electrically controlled valve.** P. B. Hamilton (E. I. du Pont Inst., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1887–1888.—The valve described is designed for use with high-flow-rate chromatographic columns to enable the eluting soln. to be changed automatically at non-working times of the day, in order to keep to a specified schedule when a sequence of soln. is being employed for column development. The valve may have other applications. K. A. PROCTOR

2394. **Densimetric analysis and graphical re-adjustment of composition for recovered ternary chromatographic solvents.** D. F. Mowery, jun. (New Bedford Inst. Technol., Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1856–1859.—The method is based on the measurement of the quantity of H_2O needed to saturate the solvent mixture and the determination of the density of the resulting saturated soln. Reference to a chart allows quick graphical re-adjustment to a predetermined composition. The method was successfully applied to the *n*-butanol - pyridine - water (10:3:3) and the ethyl acetate - *n*-propanol - water (5:3:2) systems. G. P. COOK

2395. Automatic starter for chromatograms. S. M. Martin (Div. Appl. Biol., Nat. Res. Council, Ottawa, Canada). *Anal. Chem.*, 1958, **30** (11), 1890.—The simple device comprises a stationary and a movable jaw, a solenoid-operated trigger-latch and an on-off timer. Adjustment and operation for ascending or descending chromatography are described. W. J. BAKER

2396. Micro-syringe for small liquid-volumes. S. H. Langer and P. Pantages (Bur. of Mines, U.S. Dept. of the Interior, Bruceton, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1889–1890.—The micro-syringe described and illustrated is a modification of that used by Lichtenfels *et al.* (*cf. Anal. Abstr.*, 1957, **4**, 580), and will inject 3 μl of liquid reproducibly within $\pm$ 1 to 3% and larger vol. with greater precision. A sample can be injected through a rubber tube into a plug of glass-wool above the column in a depressurised gas-chromatography apparatus. The 0·1 ml of air in the syringe serves as a flush for the needle and as a marker from which to measure zero time. W. J. BAKER

2397. The gas chromatography of micro amounts. E. Cremer and R. Haupt (Phys. Chem. Inst., Innsbruck Univ.). *Angew. Chem.*, 1958, **70** (10), 310–311.—The apparatus and time consumption necessary for complete separation of microgram amounts of mixtures of gases may each be reduced tenfold if a concn. profile with overlapping peaks is accepted. Experiments with fast-moving test substances have shown how the structure of bands, hidden by overlap, may be estimated, and have proved that the adjacent maxima remain unaffected. The shape for small amounts approximates to a Gaussian function and the individual overlapping peaks can therefore be redrawn separately and the half-intensity band widths measured. Thus, after calibration of the column with test samples, measurements from the concn. profiles of unknowns can be used in their estimation. The formula used is $m = fbh$, where m is the amount (in grams) of material, f the calibration factor, h the band height, and b the half-intensity band width. From the fact that b is an independent constant, f and b can be combined to form a new constant k, hence $m = kh$, and the slope of the curve of m *vs.* h will be constant for substance and apparatus, enabling simple determination of unknowns to be made. Further conclusions are discussed. E. G. CUMMINS

2398. Stopcock for gas chromatography. D. N. Glew and D. M. Young (Dow Chemical of Canada Ltd., Sarnia, Ontario). *Anal. Chem.*, 1958, **30** (11), 1890.—The four-way, double-oblique-bore capillary stopcock described and illustrated can be used for transferring liquid or condensable gas samples directly from a vacuum system to a gas-chromatography unit. Unlike similar devices, only one stopcock need be manipulated at the moment of admission of the sample. W. J. BAKER

2399. Analysis of fixed and condensable gases by two-stage gas chromatography. J. J. Madison (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1859–1862.—A partition column is used to separate the condensable gases, and the unresolved fixed gases emerging from the column are retained in a charcoal trap, cooled with liquid nitrogen, during the partition operation. The fixed gases are then desorbed from the trap by heating in hot water and resolved on a 25-ft. charcoal column. Analysis of a blend of H, O, N, CO, CH_4, C_2H_6 and *n*-butane by this procedure and by the mass spectrometer gave comparable results having reasonable accuracy. G. P. COOK

2400. Gas chromatograph as a methanometer in the coal industry. P. Whatmough (N.C.B. Central Lab., Shade House., Pendlebury, Manchester, England). *Nature*, 1958, **182**, 863–864.—The instrument is similar to that described previously (*Nature*, 1957, **179**, 911) except that an oil-bath containing 6·5 litres of transformer oil replaces the thermostat. Experiments with methane-nitrogen mixtures showed that the methane concn. is related linearly to peak height in the ranges 0 to 5% and 45 to 100%. The method provides a rapid and specific determination of hydrogen and methane in one sample in mine airs. H. F. W. KIRKPATRICK

2401. The obstructive or tortuosity factor in paper electrophoresis. J. T. Edward (McGill Univ., Montreal, Canada). *J. Chromatography*, 1958, **1** (5), 446–448.—The correction factor for ionic mobilities in moist paper is shown to be $(l/l')^2$, where l and l' are the lengths of the paths in free soln. and in moist paper, respectively. G. BURGER

2402. Further improvement in the apparatus for the electrophoresis of proteins. G. B. Troitskiĭ and G. B. Kobozev (Crimean Med. Inst., Simferopol, USSR). *Biokhimiya*, 1958, **23**, 869–878.—The apparatus for macro-electrophoresis (Troitskiĭ, *Ibid.*, 1951, **16**, 592; Troitskiĭ *et al.*, *Ibid.*, 1955, **20**, 431) is modified for micro-electrophoresis. The glass tube of the U-shaped vessel of the electrophoresis cell is replaced by one made of Plexiglas, which appreciably reduces electro-osmosis; the bore is reduced from $\lt$ 2 mm to 0·8 to 0·4 mm. By the use of a special optical arrangement, the 2 to 5 ml of serum required in the macro-method can be reduced to 0·3 to 0·5 ml merely by a replacement of the cells. K. R. C.

2403. Determination of radiochemical purity by paper electrophoresis. M. Mach (Res. Inst. of Radiology, Prague). *Chem. Prûmysl*, 1958, **8** (5), 236–239.—Paper electrophoresis has been used for the determination of the radiochemical purity of the isotopes ^{32}P, ^{35}S and ^{36}Cl and of irradiated Cl^-. *Procedure for ^{32}P and ^{35}S*—The simple arrangement and procedure for the separation of phosphates and sulphates [*cf.* Lederer and Ward, *Anal. Chim. Acta*, 1952, **6**, 355; *Chem. & Ind.*, 1954, (48), 1481] has been modified for 1 μl of sample with the use of 0·25 *N* HCl as electrolyte and Whatman No. 1 paper (1·5 cm × 56 cm). The procedure is complete in 2 hr. when using a potential of 5 V per cm, an initial current of 7 mA and a final current of 35 mA. *Procedure for ^{35}S, ^{36}Cl and ^{32}P*—The electrophoresis of 5 μl of a mixture of phosphates, sulphates and chlorides on Whatman 3MM paper (1·5 cm × 76 cm), in 0·25 *N* $HClO_4$ or in 0·25 *N* HNO_3, yielded good results after 2 hr., with a potential of 6 V per cm, an initial current of 12 mA and a final current of 40 mA. The activity of the electropherograms was measured by means of a Geiger tube with a thin mica window. The sensitivity of the method has been tested by analysing a soln. of ^{32}P contaminated with ^{35}S, the error being $\pm$ 6%. The separation of $^{24}NaCl$, ^{42}KCl and $^{86}RbCl$ in conc. soln. (10 to 15%) with the use of 0·25 *N* $HClO_4$ as electrolyte is also described. J. ZÝKA

See also Abstracts—**2018**, Theory and applications of gas chromatography. **2020**, Nitroprusside reagent in paper chromatography. **2022**, Ion-exchange resins in radiochemical analysis. **2028**, Use of T in paper chromatography. **2231**, Apparatus for gas - liquid chromatography. **2272**, Extinction recorder. **2350**, Gas-phase chromatography for detection of oil adulterations. **2435**, Continuous polarography of ion-exchange eluates.

Optical

2404. **Improved, single flash, continuum source for use below 2000 A.** J. A. Golden and A. L. Myerson (Gen. Elect. Co., Philadelphia, Pa., U.S.A.). *J. Opt. Soc. Amer.*, 1958, **48** (8), 548–550.—A radiation source is described which will provide a continuous spectrum from 6800 A to 1500 A. The discharge section of the source consists of a windowless 4-mm quartz capillary filled with a rare gas at reduced pressure. This is used in conjunction with fluorite optics and a vacuum spectrograph. A 15-mfd condenser at 400 V discharged through the capillary produces the flash. A single flash is of sufficient intensity to be used with either photographic or photomultiplier techniques for the study of absorption spectra in the vacuum u.v. region. B. S. Cooper

2405. **Spectral excitation in high-temperature flames as a function of sample flow.** M. R. Baker, K. Fuwa, R. E. Thiers and B. L. Vallee (Harvard Med. School, Cambridge, Mass., U.S.A.). *J. Opt. Soc. Amer.*, 1958, **48** (8), 576.—A suggestion that the sensitivity of detection of low concentrations of metals by flame spectrometry can be enhanced by increasing the flow rate of the sample is shown to be valid only within certain limits. In fact, an optimum flow rate exists at which the observed intensity of a given spectral line is at a maximum. This intensity falls off rapidly with increase or decrease of flow rate. The intensity is a function of the excitation potential of the spectral line, the flow rate and the flame temperature at that flow rate. The theoretical predictions have been verified by experiment using various metal spectra excited in a cyanogen - oxygen flame. The findings are of considerable practical importance when using high-temperature flames to achieve max. sensitivity of detection. B. S. Cooper

2406. **Special procedures in quantitative spectrographic analysis with the stylometer ST-7.** N. S. Sventitskil and Z. I. Shlepkova. *Inzh.-Fiz. Zhur.*, 1958, **1** (2), 64–68; *Ref. Zhur., Khim.*, 1958, (23), Abstr. No. 77,154.—Construct the calibration curve on the co-ordinates Δl, C, where Δl is the difference of the readings of two scales connected to the spectrometer wedges. These co-ordinates are convenient for carrying out the analysis, but do not show the actual relationship between the intensity of the line and the concn. of the element. From the known ratios of intensity in multiplets, it is easy to establish the relationship between Δl and $\log(I_1/I_2)$. From the data of eight multiplets of Zn, Mg and Cr it is established that $\Delta l = 65{\cdot}48 \times \log(I_1/I_2)$. The convenience of determining $\log(I_1/I_2)$ from the values of Δl is demonstrated by determining Si in steel. When exciting the spectrum by a condensed spark, the working curve from the lines Si 6347·0 A and Fe 6400·0 A on the co-ordinates Δl, C, is slightly curved, and a large number of experimental points is necessary for its accurate construction. When constructing the curve on normal co-ordinates from the calculated values of $\log(I_1/I_2)$, a curved graph is obtained, because of the super-imposition of the background. A straight-line graph on normal co-ordinates is obtained by introducing corrections for the background and, on the basis of this curve, a working curve for the stylometer is constructed on the co-ordinates Δl, C. In spite of the non-linearity, the graph may be drawn as accurately as desired. From an accurate working curve the probable error in determining Si in steel at a concn. of 1% is ± 2%. C. D. Kopkin

2407. **Simple micro-spectrophotometer.** D. F. H. Wallach and D. M. Surgenor (Dept. of Biol. Chem., Harvard Medical School, Boston, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1879–1882.—The instrument described allows rapid and accurate measurements to be made on 10 µl of soln. A light beam 0·4 mm in diameter is obtained from a prism monochromator. The cell, which is made from capillary tubing of 1-mm inside diameter, is positioned with the aid of a microscope, after which the transmitted light is deflected to a photomultiplier. The ratio I_0/I is measured with a balanced photomultiplier bridge circuit. K. A. Proctor

2408. **Preparation and use of large potassium bromide discs for absorption spectroscopy.** C. J. Timmons (Univ. of Nottingham, England). *Chem. & Ind.*, 1958, (34), 1110.—The framework (illustrated) was designed (before a commercial hydraulic press became available) so that a Blackhawk hydraulic ram might be used to press 16-mm discs, for use in the Unicam SP100 spectrometer, in a standard potassium bromide press, fitted with a suitable die. To minimise the sudden release of stress on the disc on extrusion from the die and to prevent distortion, the corner of the die was slightly rounded to a depth of about 0·0015 in. and the two plates and the disc were extruded together through a ring 1 in. in diam., 0·5 in. deep, by light pressure, before removal of the bottom plate. Adhesion between the disc and the wall of the die was reduced by coating the die with a silicone resin (R 205) and baking at 120° for about 1 hr. E. G. Cummins

2409. **Absorbance corrections for finite slit-width with non-uniform absorbants.** E. Back, V. F. Felicetta and J. L. McCarthy (Univ. of Washington, Seattle 5, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1875–1877.—A study has been made to determine the difference between observed and true extinctions on the assumption that the true point absorbance characteristic of the centre line of a slit is not an average extinction across the width of the slit. An equation has been derived for estimating the difference between the two extinctions, and the magnitude of this difference under various conditions is discussed. K. A. Proctor

2410. **Barium fluoride absorption cells for spectroscopy.** J. M. Gordon (Shell Development Co., Emeryville, Calif., U.S.A.). *J. Opt. Soc. Amer.*, 1958, **48** (8), 583.—Barium fluoride is fairly insoluble in H_2O and other materials injurious to NaCl and has applications as a window material for sealed liquid absorption cells. For windows 6·5 mm thick the cut-off wavelength is about 12 µ, but for 0·5-mm plates the useful wavelength is extended to 15 µ, where the transmission is about 60%. Such thin windows also have useful transmission in the u.v.

to 2000-Å region. One difficulty is in drilling holes in one of the windows for the cell to be filled and emptied. This has been satisfactorily carried out with a dental-type air blast abrasive drill.

B. S. COOPER

2411. **A double-logarithmic potentiometer for the direct linear recording of u.v. spectra in the $\log_{10}\epsilon$ scale.** H. G. Leemann and M. Kohler (Pharm. Abt. Sandoz, Basel). *Helv. Chim. Acta*, 1958, **41** (6), 1769–1771.—The construction of a double-logarithmic precision potentiometer is described, which permits the recording of u.v. absorption curves directly, as the log. of the molar extinction coeff. in a linear function, on commercially available recording spectrophotometers. N. E.

2412. **Some contributions of microwave spectroscopy to chemistry.** J. Sheridan (Univ., Birmingham, England). *Ric. Sci.*, 1958, **28** (9), 1801–1816.—Microwave spectroscopy of gases is characterised by exceptional resolving power and sensitivity. A large range of wavelengths, down to 1 mm, is used to observe such spectra in great detail with high precision. The technique is described in detail, with its use in obtaining chemically important results. These include studies of molecular geometry, quadruple coupling effects and related field asymmetries, dipole moments, and the effects of centrifugal distortion, molecular vibration, and restricted internal rotation. Because of the high resolution, chemical and isotopic analyses can be made by microwave spectra, without appreciable overlapping of absorptions. The various ways in which these developments can be applied are summarised. C. A. FINCH

2413. **Micro-modulator—a device for measuring the intensities of micro-wave absorption lines.** R. D. Mattuck and M. W. P. Strandberg (Dept. Phys. & Res. Lab. of Electronics, M.I.T., Cambridge, Mass., U.S.A.). *Rev. Sci. Instrum.*, 1958, **29** (8), 717–721.—Variations in spectroscope sensitivity, which make line-intensity measurement in microwave spectroscopy difficult, are reduced by the instrument described, in which the unknown absorption line is compared with that of a standard (diphenyltrinitrophenylhydrazil) at any frequency up to 40 kMc. G. SKIRROW

2414. **Cavity-type micro-cells for infra-red spectrometry.** R. N. Jones and A. Nadeau (N.R.C., Ottawa, Canada). *Spectrochim. Acta*, 1958, **12** (2–3), 183–191.—Semi-micro cells suitable for use with a Perkin-Elmer Model 21 or similar spectrophotometer and micro-cells for use in conjunction with a micro-illuminator in a single-beam spectrometer are described. Both types are simple to manufacture from block rock-salt. A cavity is produced by conventional drilling, followed by ultrasonic impact grinding (with a 50-W Mullard drill, type E7680/2). A cell of rectangular cross-section was found to be desirable for the satisfactory recording of double-beam spectra, a variable path-length compensating cell being employed. Sample cells of this type have been constructed with functional thickness varying between 2·0 mm and 0·1 mm. Features of the bit designed to grind out the cavities of the cells are discussed. A circular cross-section was found to be most satisfactory for the micro-cells, which were specially designed so as to achieve complete transfer of sample (10 μg) from tube to cell. Details are given of an assembly in which the micro-cell can be heated or cooled so as to effect complete evaporation of the first solvent, in which the sample was initially transferred in solution, before the addition of the i.r. transmitting solvent. E. G. CUMMINS

2415. **Potassium bromide method of infra-red sampling.** R. G. Milkey (U.S. Geol. Survey, Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1931–1933.—Interfering absorption bands originating in windows of compressed potassium bromide can be minimised by using a coarse powder and a gentle grinding technique. Such windows show less matrix absorption and absorption due to adsorbed water and the over-all light transmittance is generally higher. K. A. PROCTOR

2416. **Near-infra-red spectra with sodium chloride optics.** W. H. Washburn and M. J. Mahoney (Abbott Lab., North Chicago, Illinois, U.S.A.). *Appl. Spectroscopy*, 1958, **12** (4), 127–128.—Practical details are given for the use of a sodium chloride prism in a Perkin-Elmer Model 21 double-beam i.r. spectrophotometer to record the range 0·7 to 3·0 μ. Below 2·7 μ a correction was required to convert observed wavelength reading to true wavelength. Resolution of bands as close as 0·01 μ was obtained in the 1·2-μ region of the spectrum of oct-1-ene when run undiluted in a 1-cm cell.

P. T. BEALE

2417. **Low temperature micro-cell for infra-red study of condensed gases.** J. E. Stewart (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2073–2074.—The disadvantages of folded-path gas cells as well as the necessity of collimation in long cells can be avoided by condensing the gas into a thin film at a reduced temp. The cell described has been designed for this purpose and from 0·03 to 0·3 ml of a typical gas at atmospheric pressure is all that is required for a good spectrum. Satisfactory spectra of a single crystal $^1/_{32}$ in. square have been obtained with condensing lenses. K. A. PROCTOR

2418. **Statistical factors in X-ray intensity measurements.** M. Mack and N. Spielberg (Philips Lab., Irving-on-Hudson, N.Y.). *Spectrochim. Acta*, 1958, **12** (2–3), 169–178.—Details are given of the statistical considerations involved in the determination of the net peak intensity of a given line. The arguments are based on the assumption that the X-ray emission process is random and fluctuates according to a Gaussian distribution, for which the standard deviation is the square root of the mean. Graphical aids to the allocation of time to separate determinations of different net line intensities, so as to ensure a minimum error in the quantity of interest, are illustrated. E. G. CUMMINS

2419. **Fluorescence X-ray spectrometry. Interferences from Compton scattering from matrices of low atomic number.** C. M. Johnson and P. R. Stout (Univ. of California, Berkeley, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1921–1923.—Scattering of primary X-rays is dependent both qual. and quant. on the effective atomic no. of the matrix, on the wavelength of the incident beam and on the geometry of the source - sample - detector system. With matrices of a largely organic nature of a low atomic no., the contribution of the Compton rays is especially important and it often results in the masking of fluorescent lines and in some cases makes the identification of peaks uncertain.

K. A. PROCTOR

2420. **X-ray absorption micro-analysis with fine focus tubes.** J. V. P. Long (Cavendish Lab., Univ. Cambridge, England). *J. Sci. Instrum.*, 1958, **35** (9), 323–329.—Using an X-ray beam 1 to 2 μ in diam., transmission measurements on selected specimen areas on 2 to 10 μ diam. are possible. Comparison of transmission at different wavelengths gives quant. information on the mass thickness of elements present. Mass sensitivity is usually in the range 10^{-10} to 10^{-12} g for elements of atomic number > 15. G. SKIRROW

2421. **Electrographic colorimetry.** J. Jalůvka (Higher Pedag. School, Opava, Czechoslovakia). *Chemie, Prague*, 1958, **10** (8), 631–636.—A survey is presented of methods in which the surface of the examined material is anodically dissolved, the ions are transported through a reagent-paper to the cathode and react with the reagent. The intensity of the coloured spots formed can be compared with a standard scale. J. ZÝKA

2422. **Statistics in chemical analysis. III. Examination of results of photometric calibrations for compliance with the Beer - Lambert law.** G. Gottschalk and P. Dehmel (Osram Studienges., Berlin, Germany). *Z. anal. Chem.*, 1958, **163** (4), 273–281.—The objective testing of numerical values of photometric standard measurements for compliance with the Beer - Lambert law can be achieved by a simple linear calculation of correlation of values of ϵ (extinction coefficient) and b (concentration) with a statistical test formula. The practical application is illustrated by two examples which also indicate the influences due to the apparatus on the possibility of compliance with the law. B. B. BAUMINGER

Thermal

2423. **A convenient calorimeter heater for corrosive non-aqueous solutions.** N. L. Zutty and H. F. Herbrandson (Rensselaer Polytech. Inst., Troy, New York). *J. Chem. Educ.*, 1958, **35** (5), 260.—A calorimeter heater which is inert to nitrobenzene soln. of HCl at room temp. is illustrated and described. It consists of a threaded Teflon cylinder wound with approx. 7 ohms of No. 26 gauge, B + S, bare Manganin wire. A thin cylindrical sheath of anodised aluminium surrounding this is screwed into a hollow Teflon cylinder through which pass the current and potential leads soldered to the heating-wire. By using this heater in Brown's calorimeter (*cf. J. Amer. Chem. Soc.*, 1955, **77**, 1730), temp. changes of 0·03° corresponding to ΔH 4 kcal./mole^{-1} can be measured to a precision of 3%. O. M. WHITTON

2424. **A new method of boiling-point determination. II.** H. Böhme and R.-H. Böhm (Pharm.-Chem. Inst., Univ. Marburg/Lahn). *Arch. Pharm., Berlin*, 1958, **291** (10), 514–531.—An easily constructed apparatus which rests on a gauze over a Bunsen burner comprises three concentric glass tubes. The innermost tube (*A*) which is closed at the bottom, is about 60 cm long, and its inner diameter is about 10 mm. The sample is placed at the bottom of *A* and a thermometer (preferably an Anschütz type) is suspended over it. The middle tube (*B*), which is about half the length of *A* and acts as a heat insulator, fits loosely round *A* and is fixed to it by means of tightly wound asbestos yarn. The outermost tube, which is about as long as *B*, is a kind of sleeve and serves to guide the hot gases of combustion from the Bunsen burner along the outer wall of *B*. The top of *A* acts as a reflux. The temp. is read when the ring-like condensation boundary which creeps up the wall of *A* reaches the top of the mercury column. The apparatus is suitable not only for the identification of pure substances, but also, by manipulating the respective positions of the condensation boundary and the top of the mercury column, it is possible to detect various impurities. The method was tried out on several organic liquids and was found to be more rapid and accurate than either the D.A.B. or Pharm. Helv. methods; only 0·5 ml of sample is required for each determination. A. TESSLER

2425. **Apparatus for differential thermal analysis.** A. Blažek and J. Halousek (Inst. of Metallurgy, Acad. Sci., Prague). *Hutn. Listy*, 1958, **13** (6), 505–509.—The principle of differential thermal analysis is described. A new simple apparatus, based on a galvanometric amplifier, suitable for automatic direct recording of differential thermal analytical curves, has been constructed. Technical conditions important for correct functioning of the apparatus are given in detail. J. ZÝKA

2426. **Thermal analysis of organic compounds and its use in the analysis of isomer systems.** E. Bonauguri and G. C. Bernardi (Univ. Milan, Italy). *Z. anal. Chem.*, 1958, **162** (4), 241–256.—The true relationship between the composition of binary or ternary mixtures and their solidification-point was established by analysis of the mixtures corresponding to a finite temp. A series of general equations was derived from these analyses, suitable for the analysis of binary mixtures. The validity of these equations was tested with three isomeric nitrotoluenes. Practical details for the thermal analysis of the latter are given. S. BAAR

2427. **Automatically operated apparatus for differential and gravimetric thermo-analysis.** R. Splítek (Res. Inst. of Metals, Panenské Břežany, Czechoslovakia). *Hutn. Listy*, 1958, **13** (8), 697–705.—The thermograms are obtained by photo-registration, and, with the apparatus described and illustrated, a strictly linear temp. increase with time is not necessary. J. ZÝKA

2428. **All-quartz apparatus for the determination of fluorine by means of pyrohydrolysis.** Z. Kubec and M. Švrdlik (Spolek Pro Chem. a Hutní Výrobu, Ústí na Labem, Czechoslovakia). *Chem. Listy*, 1958, **52** (10), 2018–2021.—The apparatus described enables fluorine contents to be rapidly and simply checked and has been tested on aluminium fluoride, cryolite and CaF_2. The results were in a good agreement with those obtained with the use of platinum apparatus. J. ZÝKA

2429. **The analysis of volatile liquid mixtures by thermal-conductivity measurements on their vapours.** H. W. Linde and L. B. Rogers (M.I.T., Cambridge, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 347–353.—The composition of binary mixtures of volatile liquids can be determined by volatilisation into a stream of inert gas and measurement of the thermal conductivity of the resulting gas mixture. The construction and calibration of a thermistor bridge, designed for this purpose, are described. Results on acetone - water - nitrogen mixtures are in good agreement with calculated values. Mixtures that

show maxima or minima in the conductivity *vs.* composition curve require an elaboration of the method. H. N. S.

Electrical

2430. **Hydrostatically operated electrical switch.** E. W. Toepfer and E. W. Strock (U.S. Dept. of Agric., Washington 25, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1886.—The switch described has been devised to shut off water and power supplies to such equipment as condensers should the water-outlet flow be stopped for any reason. The switch is easily made from readily available materials. K. A. PROCTOR

2431. **Measurement of ionic strength of aqueous solutions by electrolysis.** Masaki Nakanishi (Dept. of Chem., Ochanomizu Univ., Tokyo, Japan). *Anal. Chem.*, 1958, **30** (12), 1988–1991.—The soln., slightly acidified with HCl and with bromophenol blue added, is gradually neutralised with an electrolytically generated base. The extinctions of the soln. at 435 and 595 mμ are measured and from the ratio of these extinctions the ionic strength is calculated. The calibration graph indicates a linearity of ionic strength from 0·002 to 0·02 with alkali- or alkaline-earth-metal salts of a non-reducible acid. K. A. PROCTOR

2432. **Polarography with alternating component.** R. Kalvoda (Polarographic Inst., Acad. Sci., Prague). *Chemie, Prague*, 1958, **10** (7), 529–538.—In polarography with an alternating component an arrangement similar to that of classical polarography is used; a small alternating potential in mV) at a frequency (about 50 Hz) is applied to the continuous potential which is used for the polarisation of the electrode within 0 to 2 V. The current is measured by means of an electronic voltmeter. The i *vs.* E curves obtained have characteristic peaks, the heights of which are proportional to the amount of the depolariser, and are suitable for distinguishing compounds with similar $E_{\frac{1}{2}}$. The peaks appear also when polarographing soln. containing surface-active compounds and are called tensimetric waves. These waves, which are caused by the phenomena on the surface of electrodes without electron transference, are important for the study of adsorption processes. J. ZÝKA

2433. **An improved alternating-current polarograph.** Takeo Takahashi and Eiji Niki (Inst. of Ind. Sci., Univ. of Tokyo, Japan). *Talanta*, 1958, **1** (3), 245–248.—The relationship between alternating current and the concn. of reducible substance may deviate from linear, even though the a.c. voltage superimposed on the d.c. one be kept constant. The present apparatus, "an a.c. polarograph with a.c. bridge", superimposes a small, definite a.c. voltage on the gradually changing d.c. voltage applied to the cell. When electrolytic current suddenly begins to flow, the conductivity of the soln. reaches its max. The unbalanced alternating current passes to a 2-phase balancing motor, which adjusts a variable resistance until the bridge is balanced again. P. D. PARR-RICHARD

2434. **Non-additive polarographic diffusion currents. Application to lead - (ethylenedinitrilo)tetraacetate [EDTA] system.** C. Auerbach (Brookhaven Nat. Lab., Upton, L.I., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1723–1725.—Non-additive diffusion currents are found at the electrode in solutions containing lead complexed with EDTA as well as excess of lead. Some of the uncomplexed lead is transformed into an equivalent amount of the complex while diffusing to the electrode. In the corresponding copper system the diffusion coefficients are too similar to give deviations from additivity. Analytical applications of the lead system are discussed briefly. K. A. PROCTOR

2435. **Continuous polarographic analysis of ion-exchange effluents.** R. L. Rebertus, R. J. Cappell and G. W. Bond (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1825–1827.—In the system described, a specially designed cell is used to mix the eluate and a suitable supporting electrolyte and to de-oxygenate the sample before it passes the dropping mercury electrode at a suitable fixed potential. The standard deviation of results obtained from the analysis of mixtures of Co, Cu, Ni and Mn range from about 2% for each metal ion at the 2-mg level to about 15% at the 20-μg level. K. A. PROCTOR

2436. **Supplementary equipment for an oscilloscope in oscillographic polarography.** J. Macků (Military Med. Acad., Hradec Králové, Czechoslovakia). *Chem. Listy*, 1958, **52** (5), 980–982.—Simple equipment with necessary sources and with a derivative circuit for the registration of $dV/dt = f(V)$ curves is described. The equipment also contains an arrangement for comparative measurement which enables the curves of the sample as well as of the calibration soln. to be observed simultaneously. The measurement of the position and of the depth of the incisions on the curves can also be carried out with the use of the described arrangement. J. ZÝKA

2437. **Conductimetric acid - base titrations in non-aqueous medium.** N. van Meurs (Koninkl. Shell-Lab., Amsterdam). *Chem. Weekbl.*, 1958, **54** (23), 298–303.—The method described is suitable for titration of mixtures of mono- and di-basic acids, of two dibasic acids and of a primary and secondary base. Conditions favourable are—(*i*) a low degree of solvation, (*ii*) a solvent of dielectric constant < 20, (*iii*) a small cation, (*iv*) a temperature as high as possible. The solvents used are pyridine for tetrabutylammonium hydroxide, methanol - benzene for $HClO_4$ and tetramethylammonium hydroxide. Curves of adipic acid, maleic acid and their mixture, as well of acetic acid and ethylenediamine are given. P. RENTENAAR

2438. **Analytical applications of electrical double-layer measurements.** D. C. Grahame (Dept. of Chem., Amherst Coll., Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1736–1741.—A survey of possible analytical applications of electrical double-layer measurements showed that the method closely parallels polarographic techniques, but has the characteristic of being sensitive to only a comparatively few reducible substances. A dropping gallium electrode has been successfully used and works well in non-aqueous media. The results obtained are similar to those with mercury. K. A. PROCTOR

2439. **Differential voltammetry using the hanging mercury drop electrode.** K. J. Martin and I. Shain (Chem. Dept., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1808–1810.—With this method, in which two electrolysis cells are used, each with a hanging mercury drop electrode, it is possible to determine 10^{-6} *M* soln. with increased precision and also to analyse soln. as dilute as 10^{-5} *M* without removing oxygen from the cells. Mixtures can be easily analysed by adding individual components of the mixture to the reference cell.

K. A. PROCTOR

2440. **Electrodes consisting of membranes of precipitates.** R. B. Fischer and R. F. Babcock (Dept. of Chem., Indiana Univ., Bloomington, U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1732–1736—Membranes have been prepared from inorganic ppt. such as barium sulphate with paraffin wax as an inert binder, and these can be used as potentiometric indicating electrodes. The surface electric properties of the material of which the membrane is composed can also be measured.

K. A. PROCTOR

2441. **Determination of end-points in potentiometric analyses.** F. L. Hahn (Angel-Urraza 718-303, Mexico 12, D.F.). *Z. anal. Chem.*, 1958, **163** (3), 169–181.—Procedures, illustrated by numerical examples, are given for locating the end-points in potentiometric titrations. Rules based on these are presented for carrying out potentiometric titrations.

J. H. WATON

2442. **Glass - silver electrodes in non-aqueous titrimetry.** M. G. Yakubik, L. W. Safranski and J. Mitchell, jun. (Polychemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1741–1744.—In a non-aqueous procedure for the potentiometric titration of acids, glass - silver electrodes and an electronic potentiometer are used. These electrodes respond quickly to changes in cell potential and the end-point of the titration is easily anticipated. Most acids give curves with voltage peaks; weak acids give typical S-shaped curves. It is possible to distinguish certain acidic functional groups. In the range 0·4 to 1·5 milli-equiv. the precision and accuracy are about 0·2%.

K. A. PROCTOR

2443. **Coulometric titrations in molten lithium chloride - potassium chloride eutectic.** H. A. Laitinen and B. B. Bhatia (Noyes Chem. Lab., Univ. of Illinois, Urbana, U.S.A.). *Anal., Chem.*, 1958, **30** (12), 1995–1997.—*Cf. U.S. Atomic Energy Comm.*, Rep. NP-6730; *Anal. Abstr.*, 1959, **6**, 1142.

K. A. PROCTOR

2444. **Electro-mechanical coulometer.** F. *Chem. Weekbl.*, 1958, **54** (34), 449–450.—The principle of an instrument for coulometric titration, in which a low inertia motor is used as integrator, is briefly described.

G. BURGER

2445. **Apparatus for automatic recording of coulometric titration curves.** V. Klozer (Res. Inst. of Fats and Oils, Ústí nad Labem, Czechoslovakia). *Chem. Listy*, 1958, **52** (9), 1835–1837.—The accuracy of the previously described apparatus (Čůta and Kučera, *Chem. Listy*, 1953, **47**, 1166) has been improved with the use of a new arrangement which enables the source of generating current, time-recorder and the lamp of the polarograph to be switched on simultaneously. The course of the titration is registered on photographic paper. The coulometric titration of methyl oleate with chlorine and the kinetics of the addition reaction of methyl oleate and of styrene with bromine have been studied with the use of the described apparatus.

J. ZÝKA

2446. **96,493 Coulombs.** J. J. Lingane (Harvard Univ., Cambridge 38, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (11), 1716–1723.—The techniques of constant-potential coulometric analysis and coulometric titration at constant current are evaluated theoretically. The former is more advantageous as a cathodic analytical method and the latter as a determination technique.

K. A. PROCTOR

2447. **Low-energy standards for gamma-ray spectrometry.** G. M. Matlack, J. W. T. Meadows and G. B. Nelson (Univ. of Calif., Los Alamos, N. Mex.). *Anal. Chem.*, 1958, **30** (11), 1753–1758.—Non-linear response of photomultipliers below 100 keV necessitated their calibration with many low-energy sources. Suitable standard sources were made by placing an element as target directly on a β-emitter (^{147}Pm or ^{90}Sr) when characteristic K_α radiation was generated. Suitable targets were metallic niobium, rhodium, palladium, cadmium, indium, tin, platinum, molybdenum (17·5), tantalum (57·7), copper (8·0), cobalt (6·9), manganese (5·9), vanadium (5·0), lanthanum (33·4), and lead (75 keV); certain rare-earth-element oxides were used as ceramic discs. The Tl-activated NaI scintillators were mounted directly on Dumont 6292 photomultipliers. With targets of correct thickness, the X-ray peak was symmetrical; thinner targets gave distorted peaks, and for these and also for too thick targets intensities were low. Very thin targets yielded L_α radiation. This technique provides convenient standards for checking low-energy detectors for non-linearity of response, and permits identification of radioactive elements emitting converted γ-rays.

J. P. STERN

2448. **Development and preparation of a set of gamma spectrometer standards.** L. J. Beaufait, jun., E. E. Anderson and J. P. Peterson (Tracerlab, Inc., Richmond 3, Calif.). *Anal. Chem.*, 1958, **30** (11), 1762–1764.—Eight isotopes, *viz*, ^{109}Cd, ^{133}Ba, ^{113}Sn, ^{137}Cs, ^{22}Na, ^{54}Mn, ^{65}Zn and ^{60}Co, were calibrated in terms of their γ-ray emission rate. Selection of isotopes suitable as standards is discussed and calibration curves (γ-energy *vs.* counting efficiency) are given.

J. P. STERN

2449. **Electron absorption spectrometer using an improved velocity analyser.** L. Marton and J. A. Simpson (Nat. Bureau of Standards, Washington, D.C.). *Rev. Sci. Instrum.*, 1958, **29** (7), 567–570.—In the instrument which covers the range 1 to 50 keV the principle of individually designed stages for deceleration, dispersion and re-acceleration is used. An energy resolution of 0·6 eV at 20 keV is claimed. Angular distribution data are obtained over the range $\pm$ 0·1 radian and angular resolution is better than 10^{-3} radian.

G. SKIRROW

2450. **Determination of $\beta\gamma$-activity of liquids by absorbing on [cellulose] tissue, with special reference to butex [tributyl phosphate] solutions.** F. J. Armson and T. H. English (Ministry of Works, Chemical Inspectorate, Windscale Works). U.K.A.E.A. Reprint (Decl.) WSL-R-40, 1958,

11 pp.—Up to 0·3 ml of soln. was absorbed on tissue and the wet source was counted. The precision of the method is better than that of a direct evaporation procedure. The new procedure is particularly suitable for the assay of hard β-radiation.

G. J. HUNTER

2451. **Direct-plating method for the assay of radioactive isotopes in aqueous and alcoholic samples.** H. Campbell, H. A. Glastonbury and M. D. Stevenson (Res. Lab., May and Baker Ltd., Dagenham, Essex). *Nature*, 1958, **182**, 1100.—Samples for counting are readily prepared by a modification of the method described by McCready (*Anal. Abstr.*, 1959, **6**, 497), which is free from complications due to coagulation of agar when alcoholic soln. are to be assayed. Equal vol. of 0·1% aq. agar soln. and aq. or alcoholic soln. of the sample to be counted (0·1 ml of each for a planchette 15 mm × 2 mm) are mixed in the planchette, and then dried on a hot-plate at 60°. The precision is lower than that of McCready's method, but is adequate for many purposes.

J. H. WATON

2452. **Preparation of uranium samples for mass-spectrometric analysis.** J. Slivnik and A. Zemljič. *Rep. "J. Stefan" Inst.*, 1958, **5**, 49–51.—An apparatus is described and illustrated for the fluorination of small quantities of uranium (≃ 80 mg). The time needed for the preparation of the sample is ≃ 1 hr.

N. E.

2453. **New mass-spectrometer ion-source for gas analysis.** W. Żuk (Univ. M. Curie-Skłodowska, Lublin, Poland). *Ann. Univ. M. Curie-Skłodowska, AA*, 1956, **11** (1), 1–12.—A new construction of the ion-source enables the cathode to be replaced and the anode to be cleaned without dismantling the source. An auxiliary magnetic field and a heating element are provided. The temp. is measured by a thermocouple. The linear relation between ion currents and ionising electrons and the pressure in the source is discussed as well as the method of determination of the source efficiency.

H. DMOWSKA

2454. **Ion-source for the isotopic analysis of solids.** W. Żuk (Univ. M. Curie-Skłodowska, Lublin, Poland). *Ann. Univ. M. Curie-Skłodowska, AA*, 1956, **11** (2), 13–21.—An ion-source is adapted for the mass-spectrometric analysis of volatile and non-volatile elements and compounds by addition of a 12-W furnace of 30 cu. mm capacity. The characteristics of the source and results obtained from the analysis of PbS are discussed.

H. DMOWSKA

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-} PO_4^{3-}, etc., for anions.

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